"It is a miracle that curiosity survives formal education."

Albert Einstein

"If something is boring after two minutes, try it for four. If still boring, then eight. Then sixteen. Then thirty-two. Eventually one discovers that it is not boring at all."

John Cage

"Have no fear of perfection - you'll never reach it."

Salvador Dalí

University of Alberta

LANGMUIR AND LANGMUIR-BLODGETT FILMS OF BITUMEN AT OIL/WATER INTERFACES

by

Alla Solovyev ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of

Master of Science

in

Chemical Engineering

Department of Chemical and Materials Engineering

Edmonton, Alberta

Fall 2006

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Your file Votre référence
ISBN: 978-0-494-22374-1
Our file Notre référence
ISBN: 978-0-494-22374-1

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Abstract

The main focus of this thesis was to study the interfacial behaviour of natural surface-active components of bitumen, which are believed to be major contributors to water-in-oil emulsion stability. Langmuir and Langmuir-Blodgett (LB) films of Athabasca bitumen were studied using the Langmuir interfacial trough and Atomic Force Microscope (AFM).

To study the adsorption reversibility, multiple washing experiments with fresh toluene for bitumen, maltene, and asphaltene films at the toluene/ultrapure water interface and at the toluene/recycled process water interface were performed. Asphaltenes were found to be irreversibly adsorbed at the interface. Bitumen film exhibited similar to asphaltenes irreversible adsorption after it had been washed twice with toluene. For maltene films, consecutive washings showed a progressive loss of maltenes into washing toluene.

This thesis also investigated the influence of the nature of bulk oil and water phases on bitumen film interfacial properties. It was found that the compressibility of a bitumen film increases with increasing the content of toluene in the toluene-heptane mixture used as an oil phase or acetone in the toluene-acetone mixture used as a solvent phase. Addition of acetone or sodium naphthenate to the pure water phase was found also to increase the compressibility of bitumen films. It was demonstrated that at a high pH of the water phase and in the presence of calcium ions, or when the process water was used as a subphase, the bitumen film became more rigid.

Acknowledgements

I would like to express my sincere gratitude to Dr. Jacob Masliyah and Dr. Zhenghe Xu for their excellent supervision and warm-hearted encouragement during my time at the University of Alberta. They supported, motivated, and in some cases nearly carried me to the end of this arduous road.

I have had the privilege to be a part of the oil sands research group. I greatly appreciate the time that all members of our group took to share their ideas and helpful suggestions. I specially thank Dr. Li Yan Zhang, who contributed his kind assistance throughout my work and a substantial amount of thoughtful comments on my thesis experiments and Dr. Emiliy Zholkovskiy, who has always supported me with his guidance and advice.

I particularly acknowledge the NSERC Industrial Research Chair Program in Oil Sands Engineering and its sponsors for providing the financial support for this project.

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List of Symbols

γ_0	Interfacial tension of a clean interface (N/m)
γ	Interfacial tension of an interface with a film (N/m)
θ	Contact angle
π	Surface or interfacial pressure (N/m)
ρ_p	Wilhelmy plate density (kg/m^3)
ρ_L	Liquid subphase density (kg/m^3)
A	Langmuir trough area (m^2)
F	Force on Wilhelmy plate measured by electrobalance (N)
g	Gravitational constant
L	Wilhelmy plate length (m)
TR	Transfer ratio of film deposition
t	Wilhelmy plate thickness (m)
w	Wilhelmy plate width (m)

Chapter 1

Introduction

1.1. General Introduction

Effective separation of water-in-crude oil emulsions is a major challenge for the oil industry. Water-based bitumen extraction is used to recover bitumen from oil sands. Water-in-oil emulsions are encountered at all stages during oil sands processing and transportation. After froth treatment the solvent-diluted bitumen product contains 1 – 5 μm diameter water droplets in the form of water-in-hydrocarbon emulsion. The dissolved salts in the emulsified water can cause poisoning of refinery catalyst (Yan et al., 1999; Mclean and Kilpatrick, 1997), scaling and corrosion of pipelines (Mclean and Kilpatrick, 1997; Wu, 2003). Water-in-oil emulsion can also increase the costs of transportation and refining because of the increased volume of handling (Yarranton et al., 2000; Spiecker and Kilpatrick, 2004; Zhang et al., 2003). Therefore, removing the water droplets from the solvent diluted bitumen is of great importance (Taylor et al., 2002; Zhang et al., 2005). More efficient separation of water-in-solvent diluted bitumen emulsions can help reduce the processing cost and improve the final product quality.

It is commonly believed that the accumulation of interfacially active components at the oil/water interface promotes the formation of interfacial films, which stabilize water-in-oil emulsions (Wu, 2003; Yarranton et al, 2000; Spiecker and Kilpatrick, 2004; Zhang et al., 2003; Taylor et al., 2002; Zhang et al., 2005; Sjöblom et al., 1992). After removal of the interfacial active fractions, the crude oils are not able to form stable emulsions (Zhang et al., 2005; Sjöblom et al., 1992). The film created by the interfacially active material prevents the dispersed water droplets from coalescing. Under these

conditions the oil/ water phase separation becomes extremely difficult. This thesis focuses on the adsorption of surface- or interfacially active components of Athabasca oil sand bitumen at oil/water interfaces. Monolayer properties of unfractionated bitumen and bitumen fractions are studied using a Langmuir interfacial trough and atomic force microscope (AFM).

1.2. Thesis Overview

Interfacial films created by the interfacially active components of bitumen facilitate formation of stable water-in-diluted bitumen emulsions, which are among the major problems in crude oil production. Reliable information on characteristics of oil/water interfacial films and influence of oil- or water-phase composition can help develop effective, economical and operational methods for emulsion treatment. The objective of this thesis was to study the adsorption reversibility of interfacially active components of bitumen and bitumen fractions, and the behaviour of bitumen films at oil/water interfaces at different water- or oil-phase compositions. The surface or interfacially active components of Athabasca oil sand bitumen adsorbed at the oil/water interface were studied using a Langmuir interfacial trough and atomic force microscope (AFM). Materials from the article "Langmuir Films of Bitumen at Oil/Water Interfaces" by Solovyev, A.; Zhang, L. Y.; Xu, Z. and Masliyah, J. H. published in *Energy & Fuels*, 2006 were included in this thesis. Characterization of the Langmuir and Langmuir-blodgett films of whole (but solids-free) bitumen with process water as an aqueous phase reported in this work was not found in any previously published studies.

Chapter 2 of the thesis is a description of the problem that inspired the study. A brief history of Langmuir and Langmuir-Blodgett films provided an overview on the early hypotheses, studies and observations made over the years. Theoretical background is primarily concerned with the method of studying interfacial films, interfacial film characteristics and their role in emulsions stability. This chapter also provides a brief overview of published materials that addressed the same problem or described the methodology similar to one used in this study.

The materials and experimental methods are described in Chapter 3. This chapter covers reagents and materials used in this study. Methods of treatment applied to some of the materials, such as treatment of water to be used as the subphase, solids removal and bitumen fractionation, are also described in this section.

Chapter 4 is focused on the experimental techniques and procedures. It describes the methods for preparation of Langmuir films at oil/water interfaces and deposition of Langmuir-Blodgett films onto solid substrates. It also briefly describes imaging of the deposited LB films with AFM.

The preliminary results are presented in chapter 5 to discuss the findings based on evaluation and variation of different experimental parameters, such as the nature and time of spreading solvent evaporation, amount of prepared solution, and methods of interfacial films preparation.

Chapter 6 presents a comparison of bitumen films at various oils/ultrapure water interfaces.

The series of bitumen film washing experiments presented in Chapter 7 is focused on the adsorption reversibility of interfacial components of bitumen at an

oil/water interface. Simultaneously, experiments were conducted with asphaltenes and maltenes extracted from the bitumen to understand interfacial properties of unfractionated bitumen and separate bitumen fractions. Multiple washing experiments were conducted for the mentioned films at toluene/ultrapure water interface and at toluene/ Aurora plant recycle process water interface.

In Chapter 8, the effect of chemical additives in the subphase on bitumen interfacial films is reported.

Chapter 9 as conclusions includes only a brief summary of the findings and articulates some further questions remaining to be answered on the subject.

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Chapter 2.

Background Information

The purpose of this chapter is to provide a theoretical background for the present study. A brief history of Langmuir and Langmuir-Blodgett films based on studies and observations made over past years is provided. Background information describing the principles behind the experimental methods utilized in this work is also given here. The problem that inspired this study is then described. This chapter also provides a brief discussion on published materials that addressed a similar problem or documented similar methodology. A brief description of relevant studies that have been conducted in the general area of crude oil-water emulsions and research is presented.

2.1. A Brief History of Langmuir and Langmuir-Blodgett Films

Study and understanding of interfacial films trace their history back to ancient times. In Babylonia during Hammurabi's period (18th century BC) one of the forms of foretelling was based on pouring oil on water and observing the subsequent spreading (Giles et al., 1990). Pliny the Elder and Plutarch were familiar with a method of making sea water smooth by using oil interfacial films (Giles et al., 1990). The ability of such films to calm a stormy sea was the major reason for long standing observations. To examine the phenomenon, in 18th century, Benjamin Franklin performed an experiment by placing a teaspoon of oil on water surface. Investigating the effect of oil on water, he noticed how dramatically even a little drop of oil spreads, thereby forming a very thin film of oil and producing what he called 'prismatic colors'. In 1773, Franklin, looking for

practical applications for wave-stilling effect, speculated that the oil prevented the wind from creating ripples on the water, not only preventing tiny ripples, but also stopping the wind from making existing waves larger (Giles et al., 1990; Franklin, 1774). In truth, the effect was probably more a result of surface tension that keeps the oil film flat. The phenomenon of surface tension at a liquid surface was explained by Thomas Young, a prominent English scientist (1773-1829). About a century later, in 1890 an English baron, Lord Rayleigh repeated Franklin's experiment of spreading oil on water surface. Rayleigh found that, at their maximum extension, oil films are just one molecule thick. He measured molecular size and estimated the film thickness to be between 10 and 20 Å. In his research on surface forces, Rayleigh referred to Young's work on surface tension. A German woman, Agnes Pockels, using a homemade device, was able to determine the surface tension of oil on water. Conducting experiments on the behaviour of surface tension of water, she found that the surface tension of contaminated water varies with the area of the available surface. The first surface film balance was developed by Agnes Pockels in her kitchen sink. In addition to invention of the trough technique, she was the first to use a volatile spreading solvent to assist and quantify spreading of molecules (Gaines, 1983). Having read Lord Rayleigh's work on properties of water surfaces, Agnes Pockels shared her methods and results with him. To study spreading films, Rayleigh used the device created by Pockels. Publication of Pockels' work in 1891 set the stage for Langmuir's quantitative work on monolayers (Tanford, 2004). The Nobel prize-winning American chemist Irvine Langmuir is generally accredited for designing the apparatus that could produce monomolecular, or Langmuir films. He proved the hypothesis that oil layers spread on water are one molecule thick (Gaines, 1983).

Langmuir not only was able to determine that the films were a single molecule thick, but also discovered that the molecules forming the monolayer were oriented at the water surface with the polar head-groups immersed into the water and the nonpolar hydrocarbon chains pointed upwards, away from the water surface. Langmuir was the first to investigate chemically pure substances instead of oil (Dynarowicz- Łątka et al., 2001).

In the middle of the fourth century B.C., the Egyptians were searching for a source of bitumen, which was employed to mummify dead bodies. They found such a source in the Dead Sea (Bilkai, 1984). Collecting the floating bitumen from the Dead Sea represents probably, the first attempt to transfer monolayers from water surface. In 1920, Irwing Langmuir reported the transfer of fatty acid monolayers from water surfaces onto glass slides (Langmuir, 1920). It was with the assistance of Katharine Blodgett that a technique was developed whereby monomolecular films could be deposited on a solid substrate (Gaines, 1983). During her Ph.D. research at Cambridge University, Katharine Blodgett was involved in studying the mean free paths of electrons in ionized mercury vapour. All her publications in the period from 1927 to 1932 were related to filaments and the interactions of gases or electrons with them. Langmuir's interest in monolayers on water may have been spurred by other's criticism of his earlier work and rejection of his theory on expended films. In 1932, Langmuir studied the equation of state for adsorbed films on solid surfaces. After 1932, Langmuir and Blodgett were actively involved in experimental study of films on water surface; their interest in oil films was renewed after several years away from the experimental work (Gaines, 1983). After the important work done by Langmuir and Blodgett, Langmuir

monolayers and LB-films have started to find possible applications in many fields all around the world.

2.2. Surfactants

Surface or interfacial films on the water surface or at an oil/water interface are formed by surface/interfacially active molecules (surfactants). Since Langmuir's early work, hundreds of materials have been studied in the form of monolayers formed under normal pressure and temperature. The molecules forming monolayers (including bitumen and fractions of bitumen considered in this study) generally consist of two parts, large nonpolar or hydrophobic portions – the hydrocarbon chains, and polar or hydrophilic functional groups (-OH, -COOH, etc). When such a molecule comes into contact with water, the polar group tends to interact with water, while the remaining part of the molecule tends to come out of the aqueous phase to the nonpolar phase. Hydrophilic parts of the molecules are strongly attracted to the subphase, while the other, lipophilic parts are of little solubility in the water phase but readily soluble in the oil phase. The surfactants accumulated at the interface cause a decrease in surface tension of a liquid subphase (Gaines, 1983).

Interfacial films stabilizing oil-field emulsions usually are made up of surfactants naturally present in crude oil or bitumen (Strassner, 1968).

2.3. Interfacial Pressure

Molecules in a bulk phase are surrounded by "like" molecules attracted to each other. The attractive forces are equal in all directions. At an interface, however, the molecules of different phases meet and an imbalance in the forces exists. Molecules at

the oil/water interface are subjected to interactions from molecules of oil phase and water phase. Because the molecules in both phases are situated at the interface, the orientations may not exactly be the same as when they are inside the bulk phase. Interfacial tension between two liquids is less than the surface tension of such polar liquid with strong intermolecular interactions as water. The molecules of one liquid experience attractive forces of molecules of the other liquid. Because the attractive forces are acting across the interface, the inward pull exerted by the liquid on its own molecules at the surface becomes diminished (Birdi, 2003). When a monolayer is present at the oil/water interface, the forces between the hydrophobic parts of the molecules are altered. If the area available for the monolayer is reduced by reducing the area available for molecules, the interfacially active molecules start to exert a repulsive effect on each other thereby creating a pressure called "surface" (for air/water interface) or "interfacial" pressure.

The interfacial pressure is defined as:

$$\pi = \gamma_0 - \gamma \qquad (2.1)$$

where γ_0 and γ are the interfacial tension in the absence and presence of a monolayer, respectively. The surface pressure of a monolayer at an air/water interface is assumed to lower the surface tension of a clean air/water interface due to presence of the monolayer at the interface. For the surface pressure at an oil/water interface, with γ_0 refers to the interfacial tension of pure oil/water and γ to the interfacial tension with the film present. Surface pressure is the most commonly measured monolayer property. The reduction of a clean water surface tension led Pockels, Rayleigh, and Langmuir to their conclusions about the nature of spread films (Gaines, 1983).

2.4. The Whilhelmy Plate Method of Measuring the Surface Pressure

In the Whilhelmy Plate method quantitative measurements of the monolayer properties are made by a film balance. The surface tension is measured by a Whilhelmy plate suspended from a sensitive microbalance into the surface at the center of the film. The absolute measurement of the force due to surface tension on a plate that is partially immersed in a liquid is compared with a similar absolute measurement on a clean surface. The forces acting on the plate consist of gravitational effect and surface tension acting downward which are partially balanced by buoyant effect due to the density difference of the displaced liquid. The net downward force is given by the following equation:

$$F = \rho_p g L wt + 2\gamma (t+w) \cos\theta - \rho_L g t w h \qquad (2.2)$$

For a rectangular Whilhelmy plate (Figure 2.1) of dimensions L (length), w (width), t (thickness) and density ρ_p immersed in a depth of h in a liquid subphase of density ρ_L, γ is the liquid surface tension, θ is the contact angle of the liquid on the plate and g is the gravitational constant.

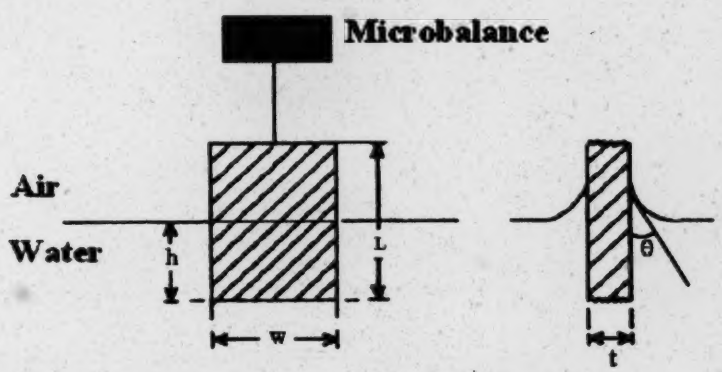

Figure 2.1. A Whilhelmy plate partially immersed into water surface.

In the case of an oil/water interface, γ is the oil/water interfacial tension. The surface pressure ($\pi = \gamma_0 - \gamma$) is determined by measuring the change in **F** for a stationary plate between a clean surface and the same surface with a monolayer present. When the thin plate is completely wetted by the liquid (i.e. $\cos \theta = 1$), Equation 2.2 yields

$$\pi = -\Delta \gamma = - [\Delta F / 2(t+w)] \qquad (2.2a)$$

(Gaines, 1983).

The Whilhelmy Plate method is commonly used for measurements of monolayer properties. The Whilhelmy plate is a thin plate usually made of glass, quartz, mica, platinum or paper. The Whilhelmy plate should be maintained completely wetted by the liquid. In this work, the interfacial pressure was measured with a Wilhelmy plate made of filter paper, Whatman 1 CHR suspended from a sensitive microbalance and partially immersed in the water subphase. A device utilised for measuring monolayer properties will be described further. In this study, continuously monitoring and recording the interfacial pressure (π) as a function of the available monolayer area (A), interfacial pressure-area (π -A) isotherms were obtained.

2.5. Surface Pressure-Area (π -A) Isotherms

Studying monolayer behaviour, Henri Devaux wrote that molecules in a monolayer could exist in different states that are analogous to three-dimensional gases, liquids, or solids. He showed the possibility of qualitative estimation of monolayer fluidity by dusting talc particles onto the film (Gaines, 1983). The different configurations of surface active molecules forming a monolayer can be distinguished by the increase in surface pressure during the monolayer compression. Figure 2.2 shows generalized surface pressure-area (π-A) curve obtained upon monolayer compression

with various states and transitions, which may occur on a Langmuir film compression. This curve has a stepwise character, which witnesses the presence of different compressibility states. When the area available for the monolayer is sufficiently large, the molecules in the monolayer are far apart and have relatively little effect on each other. The hydrophobic tail groups of the molecules lie nearly flat at the water surface. Under these conditions,the monolayer is said to be in the gaseous state. This region of the curve is characterised by high area (A) values and low surface pressure (π) values, marked as region AB in Figure 2.2. Compression of the film leads to decreasing A and increasing π. As the monolayer is compressed to a certain critical π value, at point B, the monolayer begins to enter the liquid-expanded state. In the region of transition between the two states (a small plateau in figure 2.2) the molecules of the gas and liquid expanded states co-exist. At the transition between two states, a plateau may not necessary be entirely flat, but the slope would be less steep than that for the neighbouring regions of the isotherm. At the liquid-expanded state, the tail groups of the molecules begin to lift away from the water surface. Under continued compression, the monolayer enters a liquid condensed state (BC) at which the molecules arrange to allow chain groups to pack closely. When monolayer is subjected to increasing surface pressure, the molecules can reach their closest possible packing. This state of a monolayer can be thought of as two-dimensional solid. At the solid state, the monolayer is highly incompressible. After the sharp transition, at point C, the film changes to an incompressible form, shown by extremely steep region of the curve, CD. Further monolayer compression can result in film collapse. The film collapse pressure, D, is the highest pressure to which a monolayer can be compressed. It is impossible to increase

the surface pressure any further. Under this condition, the area decreases if the pressure is maintained constant, or the pressure falls if the film is held at constant area, region DE. When collapse occurs, the molecules are forced out of the monolayer forming three-dimensional aggregates (Gaines, 1983)

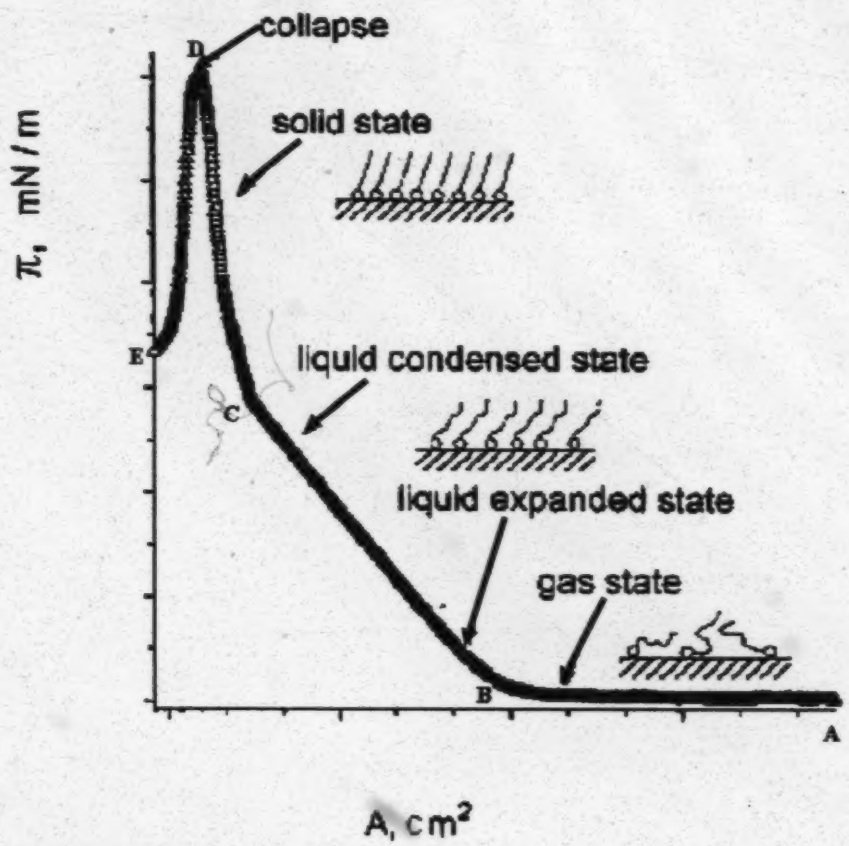

Figure 2.2. Generalized surface pressure-area (π -A) isotherm for a surface active substance, showing various states and transitions, which may occur on a Langmuir monolayer compression.

The monolayers of materials examined in this study display the above described regions. However, there are no sharp transition points between different monolayer

states, indicating that the studied materials are composed of various chemical species with varying phase transition points.

2.6. Role of the Interfacially Active Materials in Stabilization of Water-in-Crude Oil Emulsions

Understanding emulsion behaviour is directly related to the understanding of interfacial properties of natural surface active compounds, which stabilize water-in-bitumen emulsions. Each water droplet is encapsulated in an envelope formed by surfactants with the polar-hydrophilic part of the molecules attracted to the aqueous phase and the hydrophobic end extending to the oil phase. The accumulation of interfacially active molecules at a bitumen-water interface produces a mechanically strong film that resists the coalescence of droplets (Wu, 2003; Yarranton et al, 2000; Spiecker and Kilpatrick, 2004; Zhang et al., 2003; Taylor et al., 2002; Zhang et al., 2005; Sjöblom et al., 1992) (Figure 2.3). Under such conditions, even when the distance between the droplets is diminished due to a net attraction between the droplets, the individual droplets maintain their identity. To make droplets coalesce, the thin film separating the dispersed droplets should be destroyed (Sjöblom, 1992).

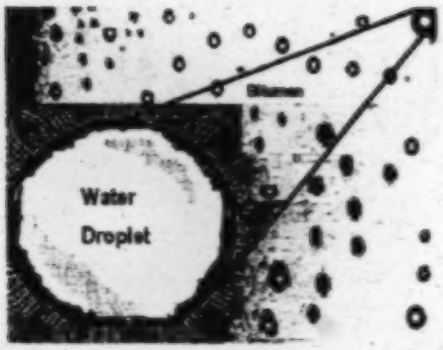

Figure 2.3. Schematics of a water-in-bitumen emulsion. Water droplet stabilized by interfacially active materials accumulated at the water droplet surface.

Interfacial behavior of different bitumen or crude oil fractions has been the subject of numerous studies. Crude oil is a complex mixture of molecules with different molecular structures. Because of the wide variety of compositions of crude oils having different origins, characterization of individual molecular type is difficult. Instead, different fractions based on solubility classes are often used for the characterization. A common practice is to separate a crude oil or bitumen into four fractions: saturates (S), aromatics (A), resins (R) and asphaltenes (A), to obtain the so-called SARA fractions, as shown schematically in Figure 2.4. The asphaltene fraction is defined as a group of molecules that are insoluble in light alkanes (such as heptane) and soluble in toluene (Speight, 1991). After removal of asphaltene via precipitation, the deasphalted fraction, is referred to as maltenes. Maltenes consist of saturated hydrocarbons, aromatics, and resins (Mclean et al., 1998).

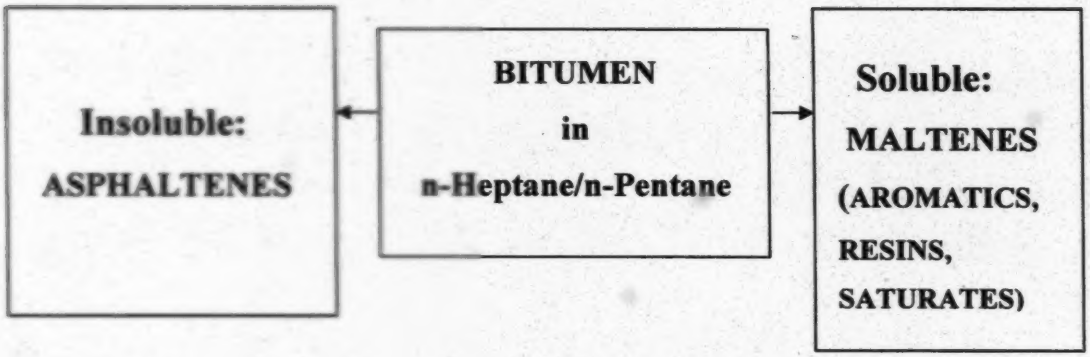

Figure 2.4. Schematic representation of the bitumen SARA fractionation.

Studying stabilization and destabilization of water-in-crude oil emulsions, Urdahl and Sjöblom (1995) concluded that the interfacially active asphaltenes and resins are responsible for emulsions stabilization. Model systems stabilized by extracted interfacially active components were found to have stability properties similar to that of the actual crude oil emulsions.

Mohammed et al. (1993) reported that asphaltenes are the dominant contributors to stabilizing water-in-oil emulsions. They showed that asphaltenes and their mixtures with resins stabilize water-in-oil emulsions. The resins themselves could not stabilize emulsions at the same level since the films formed by a resinous material are not sufficiently rigid to prevent coalescence.

Using a Langmuir trough, Ese et al. (1998) studied the film-forming properties of asphaltenes and resins that were extracted from different crude oils. They found that asphaltenes pack closer and form more rigid films than resins at an air/water interface. A comparison between asphaltenes and resins showed that resin films are highly compressible, and the resin molecules do not aggregate to the same extent as asphaltenes.

Yan et al. (1999) studied the role of various Athabasca bitumen components in stabilizing water-in-diluted bitumen emulsions. They observed that the capability of stabilizing water-in-diluted bitumen emulsions was high when asphaltenes were present. When the asphaltene was removed, the ability of diluted bitumen to stabilize emulsified water decreased. Although deasphalted bitumen acted as a poor emulsion stabilizer, interfacial tension measurements revealed the presence of surface-active components.

Zhang et al. (2005) studied adsorbed monolayers at the oil/water interface of sub-fractions and unfractionated asphaltenes extracted from Athabasca bitumen. In their study, heptol, a mixture of heptane and toluene, with varying heptane to toluene volume ratios was used as the oil phase. The Langmuir trough experiments showed that the aromaticity of the crude medium is a prime factor determining the state and rigidity of the asphaltene monolayers at oil/water interfaces. With increasing heptane content in heptol, both the highest attainable interfacial pressure and the mass of adsorbed material increased. Although the bulk asphaltene material is known to be completely soluble in heptol at a heptane to toluene volume ratio of 0.5, an asphaltene monolayer still forms at the heptol/water interface. From their study, a conclusion was drawn that asphaltene molecules are strongly adsorbed at the oil/water interface and do not leave the interface.

Subsequently, Zhang et al. (2005) used the Langmuir trough technique to study the effect of replacing the initial toluene top phase with a fresh toluene top phase on the interfacial behavior of an asphaltene monolayer at the toluene/water interface. The initial toluene was found to contain a negligible amount of asphaltenes, indicating that the asphaltenes did not migrate to the bulk toluene phase and the amount of asphaltene at the interface remained unchanged. The asphaltene monolayer was found to remain at the

toluene–water interface after several dilutions (washings of the monolayer) with fresh toluene.

Freer and Radke (2003, 2004) employed a model oil system consisting of asphaltenes precipitated from a heavy crude oil and dissolved in toluene to study the relaxation mechanisms of interfacial material using the oscillating pendant drop technique. It was found that the dynamic interfacial tension for the model oil system was similar to that observed for the original crude oil. Washing experiments, i.e. removing the organic phase and replacing it with fresh toluene, were performed after aging the interface for 24 h. While compressing the model oil/water interface, they visually observed an interfacial skin. Washing away the reversibly adsorbed surface-active species was found to increase the interfacial tension only by 1.5 mN/m. They concluded that, although toluene is a good solvent for asphaltenes, the majority of asphaltenes are irreversibly adsorbed at the toluene/water interface.

It had been shown that interfacial activity of crude oil components is a key factor determining the degree of formation and stability of water-in-crude oil emulsions. In the above cited papers, separate bitumen-fractions such as asphaltenes and resins had been studied with respect to the oil/water interface. Czarnecki and Moran (2005) discussed oversimplification of the common paradigm which claims that water-in-oil emulsions are stabilized by asphaltenes alone. This paradigm can not be proven by results of studying petroleum emulsion stabilization using approach based on the removal of one (usually asphaltenes) or several oil fractions and investigation of their ability to stabilize emulsions. These methods exclude the possibility of competition for the oil/water interface among various interfacially active fractions separated from bitumen. They

proposed an alternative model of water-in-oil emulsion stabilization that is based on three major assumptions: (1) the asphaltene-like, interfacially active material adsorbs slowly and irreversibly and forms rigid skins, (2) other surfactant-like species of bitumen adsorb fast but reversibly (at high concentrations fully covering the available interface), and (3) drastic changes in interfacial material composition are brought on by critical dilution (Czarnecki and Moran, 2005).

In the present work, we study adsorption at the oil-water interface of unfractionated (but solids-free) bitumen at low concentrations of bitumen in organic solvent. In this research, the adsorption of surface or interfacial active components of bitumen at an oil/water interface was studied using an interfacial Langmuir-Blodgett trough. Efforts were made not to overload the available interface by using small amount of solutions at low concentrations, thereby maintaining low concentrations of the interfacial material. A series of washing experiments, by repetitive removal of the solvent phase and replacement of it with a fresh one, was performed to study the reversibility of adsorption of surface active components from bitumen at an oil/water interface. Simultaneously, experiments with asphaltenes and maltenes were conducted to verify the difference in the interfacial behaviour of unfractionated bitumen and bitumen fractions.

2.7. Effect of the Organic Phase Composition on the Interfacial Film Properties and Emulsion Stability

The composition of the solvent phase has significant effect on the state and rigidity of interfacial films. The hydrocarbon side chains of interfacially active

molecules have different conformations when they are embedded in different solvents with varying aromaticity (Walker et al., 1998).

Taking into consideration the concept that asphaltene solvency is directly responsible for emulsion stability, McLean et al. (1997) studied the effect of changing the aromaticity of the crude medium by blending solvents of varying amounts and aromaticity with different crude oils. Using n-heptane as the solvent phase caused emulsion stabilization due to the reduced molecular solubility of the asphaltene fraction in the crude oil. Increasing toluene content in the solvent phase helped destabilize the emulsion. The results are to be expected, since asphaltenes, by definition, are a solubility group of materials soluble in toluene, but insoluble in heptane (Zhang et al., 2005).

In the study of emulsions produced from Arab Heavy oil, other than heptane and toluene, solvents such as benzene, ethyl-benzene, tetra-butyl-benzene, xylene, cumene, and cymene were also utilized. The amount of the resolved water increased with increasing amount of solvent added. It was evident from the experimental results that the more aromatic a solvent is (with the highest aromatic carbon content), the more effective it is in resolving an emulsion.

Zhang et al. (2005) conducted experiments testing the effect of 2-propanol addition into the bulk toluene top phase on interfacial behaviour of asphaltenes. Their goal was to find a way to destroy the asphaltene film formed at a toluene/water interface. The results obtained from experiments utilizing a Langmuir trough and AFM showed that 2-propanol molecules, most likely penetrated into the asphaltene monolayer, weakened the asphaltene molecular interactions and led to decreased rigidity of the

interfacial film. As a part of current work, the effect of acetone addition to the toluene top phase on bitumen and asphaltene films was studied.

Investigating the role of asphaltenes and resins in stabilizing model water-in-crude oil emulsions, Gafonova et al. (2001) found that the addition of a good solvent can help reduce both the amount of the adsorbed asphaltenes and emulsion stability. The stability was assessed from the amount of water resolved after heating and periodic centrifugation of the emulsion. In a poorer solvent, asphaltenes, which caused emulsion stabilization, were removed by precipitation. As a result, emulsion stability decreased.

Zhang et al. (2005) studied adsorbed monolayers at an oil/water interface of sub-fractions and unfractionated asphaltenes extracted from Athabasca bitumen. In their study, heptol, a mixture of heptane and toluene, was used as the oil phase with varying heptane to toluene volume ratios. The Langmuir trough experiments showed that the aromaticity of the crude medium is a prime factor in determining the state and rigidity of asphaltene monolayers. With increasing heptane content in heptol, both the highest attainable interfacial pressure and the mass of adsorbed material increased.

Various experiments have shown that aromatic solvents interact with the interfacial asphaltene films thereby modifying their properties. Further tests showed similar behaviour for the whole solids-free bitumen films. In this thesis, experiments were conducted with different content of toluene in heptol (mixture of heptane and toluene).

2.8. Effect of pH and Composition of the Aqueous Phase on Interfacial Film Properties and Emulsion Stability

The surface active fractions of bitumen include a large variety of chemical species with acidic and basic functional groups. A number of studies have identified the importance of the composition and pH of the aqueous phase and possible interaction between chemical additives and components of the interfacial films.

Studying the influence of pH on stability and dynamic properties of asphaltenes and other amphiphilic molecules at the oil/water interface, Poteau and Argillier (2005) found that at high or low pH, the functional groups of asphaltene molecules become at least partly charged, increasing their hydrophilic nature and hence their interfacial activity. The results of micropipette experiments indicated little water droplet coalescence at high or low pH. Similar behaviour was observed from the experiments with mixtures of asphaltenes and maltenes. For mixtures, the phenomenon was more pronounced at high pH. The obtained results on microscopic properties of the interface and the macroscopic behaviour of the emulsion were well correlated.

When various crude oils were demulsified at different water phase pH, it was shown that different crude oils have different optimum pH. Films formed by asphaltenes were stable at an acidic pH, while films formed by resins were stable at a basic pH (Strassner, 1968).

In their study with a Langmuir trough of water-in-crude oil emulsions from the Norwegian continental shelf, Nordli et al. (1991) analyzed the influence of electrolytes, pH, and chemical additives on the monolayer properties of the interfacially active crude

oil fractions. They presented the chemical analysis of the interfacially active fractions of some samples, which were found to consist of hydrocarbon polymers with mean molecular weight between 900 and 1500. Some of the polar groups were ionized at low pH. When the distilled water subphase was replaced by synthetic formation water of higher salinity, the recorded surface pressure-area isotherms shifted towards larger specific areas. In their previous work Nordli et al. had shown that solvent-like molecules such as medium chain alcohols and amines destabilize water-in-crude oil emulsions. Their study also showed that benzylalcohol and octylamine expand the monolayer, while 1-butanol contracts it when added to the subphase. All three additives were found to interact with the interfacial film. Moreover, at sufficiently high concentrations they destabilize the emulsion by displacing the surface active fractions.

In this work we studied the effect of pH and replacement of the distilled water subphase with process water or water with defined amounts of chemical additives as means to understand the effect of chemical additives on the adsorption of bitumen interfacial material.

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Chapter 3

Experimental Materials and Reagents

This chapter describes reagents and materials used in this study. It also covers methods of treatment applied to some of the used materials.

3.1. Solvents

ACS-grade toluene (99.5%), Optima-grade toluene (99.8%), HPLC-grade *n*-heptane (99.6%), HPLC-grade chloroform and HPLC-grade acetone were all purchased from Fisher Scientific Canada and used as received without further purification. Optima-grade toluene and HPLC-grade heptane were used as solvent phase in Langmuir interfacial trough experiments, while Optima-grade toluene (99.8%) was used as a spreading solvent (unless otherwise stated).

3.2. Removal of Suspended Solids from Bitumen

Vacuum distillation feed bitumen was supplied by Syncrude Canada Ltd. Solids-free bitumen was obtained by dilution of bitumen with ACS-grade toluene at a toluene/ bitumen ratio of 5:1 followed by centrifugation at 20,000 rpm (35,000g) for 30 minutes. After centrifugation, toluene was removed from the bitumen through natural evaporation in a fume hood for one week.

The prepared solids-free bitumen was dissolved in Optima-grade toluene to a concentration of 1 mg/mL to prepare a stock bitumen-in-toluene solution. The prepared bitumen-in-toluene solution was filtered with a 0.2 μm Teflon membrane to further

remove any remaining fine solids that were not completely removed by centrifugation. The prepared bitumen is referred to as "solids-free bitumen."

3.3. Separation of Asphaltenes

Asphaltene separation was conducted following the procedure described in detail by Zhang et al. (2005). Briefly, asphaltene was extracted from solidS-free bitumen by precipitation with heptane at a heptane/bitumen volume ratio of 40:1, followed by washing with an excess amount of heptane. The washing process was repeated several times until the washing heptane supernatant became colorless. The mass of the extracted asphaltene was approximately 15 wt % of the original bitumen. Maltene fraction was obtained from the deasphalted bitumen by natural evaporation of heptane in a fume hood for 1 week. To prepare asphaltene-in-toluene and maltene-in-toluene stock solutions, maltenes and asphaltenes were dissolved in Optima-grade toluene to a concentration of 1 mg/mL (unless otherwise stated).

3.4. Preparation of Aqueous Subphase

There was a significant difference in the interfacial behaviour of bitumen films with respect to the type of liquid to be used as a subphase. The temperature of any liquid used as a subphase was maintained constant at +20°C (with an accuracy of ±0.2°C) using a thermal bath circulator. The following types of an aqueous subphase were used in this study:

(1) Ultrapure water (resistivity 18.2 MΩ cm) was obtained from a Millipore Milli-Q system.

(2) Aurora plant recycle process water was supplied by Syncrude Canada Ltd. (Results from chemical analyses of the recycle process water are listed in Table 7.1.) The water was allowed to stand for an extend period to allow the coarse solid particles settle before filtration through a series of filters with decreasing pore sizes from 200 μm to 0.1 μm (Whatman PTFE (polytetrafluoroethylene) filters).

Solutions prepared using ultrapure water:

(a) For experiments that required pH adjustment, sodium hydroxide, NaOH (0.1 M) and hydrochloric acid, HCl (0.1 M) were used.

(b) Calcium chloride (Puratronic 99.9965%) was added to water to make a solution with 600 ppm Ca^{2+}, and the water pH was adjusted to 8.5.

(c) Naphthenic acid sodium salts were added to water to reach a final concentration of 1 g/L.

3.5. References

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Chapter 4

Experimental Methods and Techniques

In this study, an interfacial Langmuir trough and atomic force microscope (AFM) were used to prepare and study all the films tested. Langmuir trough is a convenient tool for the formation of oil/water interfacial films. It can also be used as a tool for Langmuir-Blodgett or LB film deposition (films deposited on solid substrates) to study molecular state at the interface by AFM imaging.

4.1. Langmuir Trough

Langmuir trough experiments were performed with a computer-controlled KSV Langmuir interfacial trough (KSV Instruments, Finland), which is shown in the schematic drawing (Figure 4.1). The trough system consists of a shallow rectangular trough which has two compartments, a lower compartment for the aqueous subphase and an upper one for an oil top phase. Two moving barriers are placed at the edges of the trough.

The maximum area between the inner edges of the barriers at their full expansion is 166 cm^2. The trough and the barriers are made of hydrophilic polyacetal, Delrin. A given number of molecules are placed on aqueous suphase between the barriers. Film leakage is avoided by using hydrophilic material for the trough barriers. By moving the barriers at constant rate of 10 mm/min per barrier, the molecules at the surface or interface are compressed symmetrically. Several compression rates tested in this work (3mm/min, 5mm/min, 10mm/min) resulted in interfacial pressure-area (π–A) isotherms within the acceptable experimental error. The compression rate for the studied films was

chosen to be 10 mm/min. Barriers have holes to allow the top phase to flow through freely. Movement of the barriers is controlled by a stepping motor operated manually or under computer control. KSV Device Server Software is used to control the position of the barriers and continuously monitor the surface pressure as a function of the trough area. At the beginning of each test, the experimental conditions (trough area, temperature, and pH of the subphase; volume, density and molecular weight of the studied substance) are recorded into the experimental setup page. The surface pressure is measured with a Wilhelmy plate (filter paper Whatman 1 CHR) suspended from a sensitive microbalance and partially immersed in aqueous subphase in a direction parallel to the barriers. The barriers' position at maximum expansion is zeroed at the beginning of each test. The temperature of the aqueous subphase is controlled by the water bath circulator. The compression curves describing the monolayer behaviour are recorded at constant temperature ($20 \pm 0.1°$ C). Data of the isotherms (pressure versus area) can be exported.

For preparation of Langmuir-Blodgett films (LB films), there is a dipping well in the middle of the trough. The solid substrate for LB film deposition can be attached to a holder that can be moved upwards or downwards by a displacement mechanism operated manually (when accuracy is not vital) or under computer control. A sketch of the setup is given in Figure 4.2.

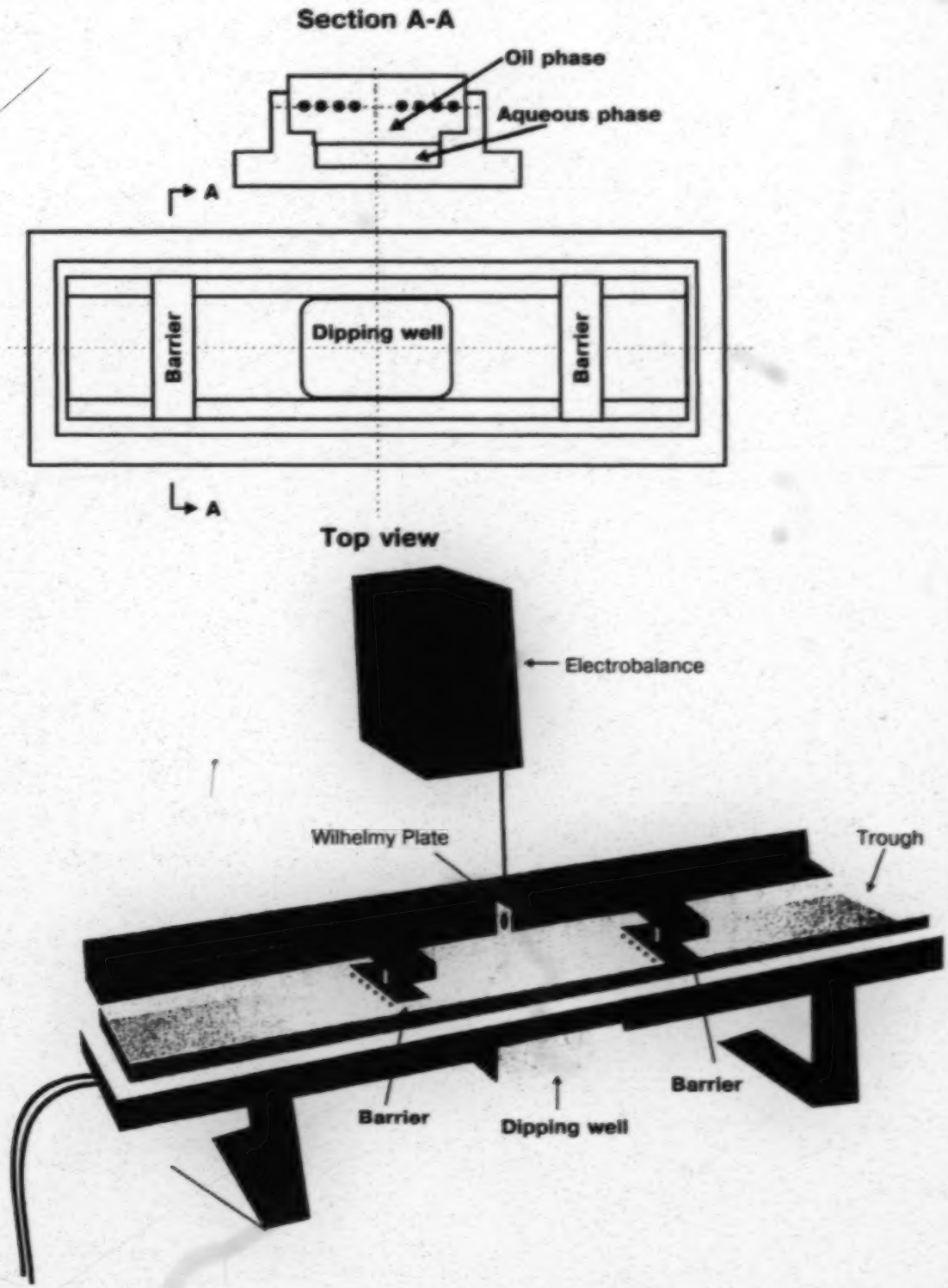


Figure 4.1. Schematic representation of Langmuir interfacial trough

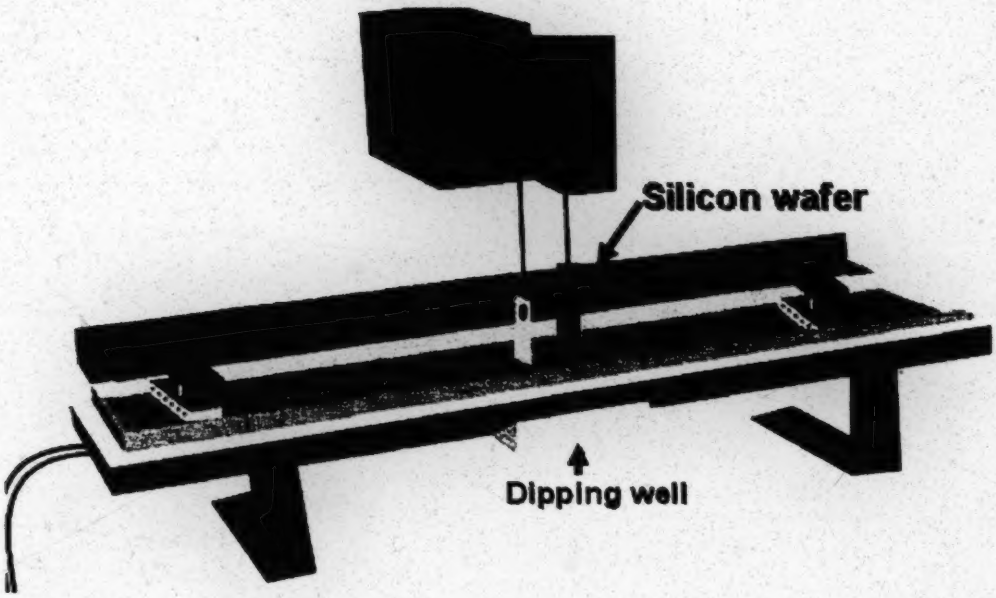


Figure 4.2. Schematic representation of Langmuir-Blodgett interfacial trough

4.2. Trough Cleaning and Maintenance

While conducting experiments, one must take into account the high sensitivity of the Whilhelmy Plate method. Artifacts in the isotherms recorded can be attributed to various factors among which is the impurity of the prepared subphase, caused by unclean trough/dust contamination and/or partial deposition of a film from a previous experiment on a Whilhelmy plate. Originally, the trough is enclosed in a vented chamber to minimise possible dust contamination. At the start of each run, the trough and the barriers are rinsed with solvent such as n-heptane under the fume hood and cleaned thoroughly with acetone-soaked Texwipe wipes, followed by wiping with dry Texwipe wipes. The dry trough is then rinsed several times with ultrapure water. The water is

removed with the suction pipette connected to a vacuum line before filling the trough with the testing liquid subphase for an experiment. Powder-free gloves are worn while cleaning the trough. A chromatography paper Whilhelmy plate is changed often to ensure cleanliness. Before each measurement, the purity of the subphase is checked by rapid compression of the air/water interface to a small trough area. The water surface is cleaned with a pipette connected to a vacuum system. The cleaning procedure is repeated if the surface pressure obtained upon compression to a small trough area is higher then 0.10 mN/m. Each experiment is repeated several times without any changes in experimental conditions to ensure reproducible results.

4.3. Preparation of a Langmuir Film at an Oil/Water Interface

An interface is a boundary region between two phases (Gaines, 1966). Oil/water interface is important in connection with extraction kinetics, emulsions (oil-in-water and water-in-oil), and surfactant solutions. The difference in its behaviour can be explained by different solvency of the oil phase for the hydrophobic residues of the amphyphilic molecules. All the experiments were started with spreading molecules at the interface. In the lower compartment, a liquid subphase (for example ultrapure water) at a volume of 120 mL was added. To prepare the interfacial film, a prepared solution was spread onto a clean water surface. To do so, a drop of the spreading solution was formed on the tip of a micro syringe and then lowered to touch the surface. The syringe was then raised, a new drop formed, and the process was repeated until all the solution was spread. The spreading of the solution followed by evaporation of the spreading solvent (toluene) for

a given period of time (according to the results of the preliminary experiments, given in the following section, 10 minutes were allowed for solvent evaporation). For the case of film preparation at the oil/water interface, 100 ml of organic solvent was poured along a glass funnel to cover the entire surface. After a waiting period of 30 minutes, the interface was ready for compression. By moving the barriers (which contained holes to allow the top phase to flow through without disturbing the prepared interface), the prepared monolayers were compressed symmetrically. (In case of monolayer preparation at the air/water interface, the barriers were compressed immediately after the spreading solvent evaporation.)

Asphaltene monolayers were prepared by dropwise spreading 15 μL of the prepared asphaltene-in-toluene solution (1 mg/mL); and maltene films were prepared by spreading 85 μL of maltene-in-toluene solution (1 mg/mL). For the series of experiments with bitumen films for comparison with asphaltene and maltene films, the bitumen monolayers were prepared by spreading 100 μL of the prepared bitumen-in-toluene solution (1 mg/mL) on the water surface. The spreading volumes were chosen to ensure a fair comparison among bitumen, asphaltene and maltene films to reflect the actual content of asphaltene and maltene in bitumen. At these volumes and employed concentration of 1 mg/mL, it was ensured that the molecules do not completely cover the water/solvent interface over the initial expanded trough area. A concentration of the spreading solution was determined with high accuracy since evaporation of a volatile solvent can lead to surprisingly large changes (Gaines, 1966). All the solutions used in this work were freshly prepared to avoid solvent losses by evaporation during solution storage.

4.5. Preparation of Silicon Substrates

Hydrophilic silicon wafers were used as the solid substrates for bitumen, asphaltene and maltene film deposition. Silicon wafers were cut by a glass cutter into square pieces. To avoid touching wafers with hands, tweezers were used to handle them. Prior to deposition, the silicon substrates were cleaned following a multi-step process. They were first soaked overnight in detergent solution, then in sulphuric acid (H_2SO_4), rinsed with Milli-Q water, and finally placed for 15 minutes in a bath with hot solution of one part of ammonium hydroxide (NH_4OH), one part of hydrogen peroxide (H_2O_2) and five parts of water (H_2O) to remove any organic residues. After removal from the bath, the substrates were rinsed thoroughly with ultrapure water and then stored in clean ultrapure water until being used. Immediately prior to deposition, the silicon substrates were blow-dried with a high velocity stream of high purity nitrogen gas. The prepared hydrophilic silicon wafers were used as solid substrates for Langmuir-Blodgett film deposition.

4.6. Deposition of Langmuir-Blodgett (L-B) Films from an Oil/Water Interface

A Langmuir film balance (Figure 4.2) is also used as a tool for monolayer deposition. The deposition of a Langmuir-Blodgett (LB) film can be conducted in a vertical or horizontal (Langmuir –Schaefer) mode. Horizontal transfer has been applied to films that cannot maintain a constant surface pressure. In the traditional vertical dipping mode, the substrate is immersed into the water phase and then raised through the monolayer-covered interface. There is a dipping well in the middle of the trough. The

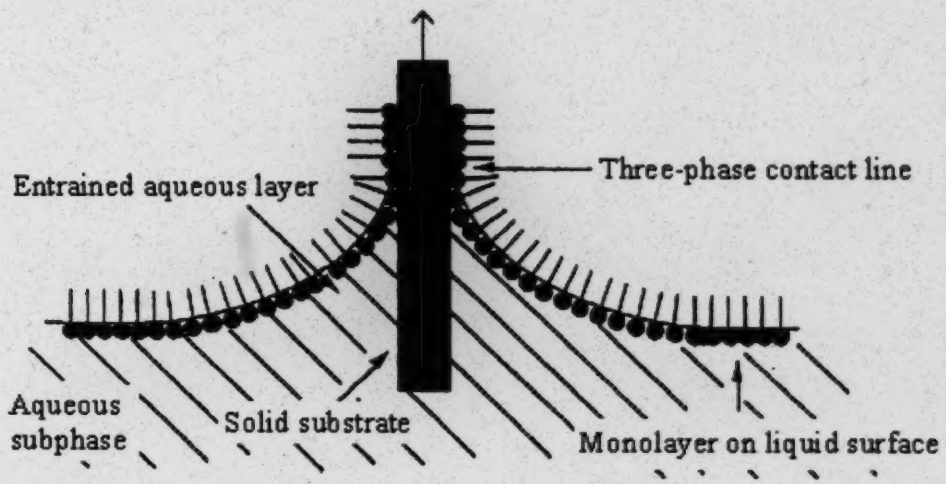
solid substrate for LB films deposition can be attached to the holder that can be moved upwards or downwards.

The monolayer was deposited as the solid substrate moved upward (Figure 4.3). The transfer of a single layer onto an initially cleaned hydrophilic substrate is often performed by immersing the substrate prior to spreading of the monolayer. The film at the interface is then compressed to the desired surface pressure. It is desirable to maintain the pressure constant while the substrate is being drawn up through the interface. The LB deposition is traditionally carried out at the state of "solid" monolayer. Keeping barriers at fixed position allows one to maintain a constant interfacial or surface pressure at a sufficiently high value so that strong attractions between the molecules in the monolayer help avoid monolayer falling apart during the deposition (KSV Instruction Manual for Windows, 2000). A monolayer is transferred on the upward pass through the interface. The monolayer transfer is described by the transfer ratio, defined as the decrease in area of the monolayer divided by the area of the substrate. A transfer ratio of unity is an ideal transfer; and close to unity would indicate a uniform transfer. Transfer ratios much below unity (0–0.3) would indicate partial transfer, and those much greater than unity, as high as 3–5, indicate significant monolayer collapse or structural relaxation during the transfer process (Stine and Moore, 2001).

In this work, monolayers of interest were transferred from an oil-water interface onto hydrophilic silicon wafers by LB deposition. A silicon wafer was immersed in the aqueous subphase before spreading molecules of interest. After spreading molecules, the aqueous subphase was fully covered by oil phase. Barriers were compressed up to a surface pressure of 10 mN/m. Keeping the surface pressure constant (at 10 mN/m), film

was deposited as the substrate, a silicon wafer, was moved vertically upwards through the monolayer covered oil-water interface. The silicon wafer was held parallel to the barriers and lifted at a constant rate of 5mm/min. The obtained transfer ratios were approximately unity.

The deposition process is schematically shown in Figure 4.3.



.**Figure 4.3.** Deposition of a monolayer from the oil/water interface

4.7. AFM Imaging of the LB Films

In this work the deposited LB films were studied with an atomic force microscope (AFM). Studying the deposited films can provide the information on molecular structure in the film. The AFM allows direct visualisation and imaging of molecular structures ranging from several nanometres to several microns thereby making the AFM an attractive technique for LB film characterisation.

During operation of the AFM, the sample of interest was placed under a sharp tip at the end of an AFM cantilever. Figure 4.4 is a general schematic representation of an

AFM system. The AFM operates by measuring attractive or repulsive forces between a tip and the sample. In the repulsive "contact" regime, the tip is dragged over the sample surface and the AFM measures repulsion forces between the tip and the sample. In the "non-contact" regime, the tip remains at a distance from the sample surface where the attractive forces dominate (DeRose and Leblanc, 1995). AFM images of LB films shown in this thesis were obtained in the tapping mode, which is a compromise between the contact and non-contact regimes. In the tapping mode, the cantilever oscillates at a very high frequency (260–320 kilohertz) as it scans the sample surface. The oscillation amplitude changes, due to the change in atomic topography of a sample surface, are used as signals for image formation. As the cantilever bends, a laser beam directed onto it is reflected at a different angle. The reflected beams are captured and converted into electrical signals by position-sensitive photo-detector (Figure 4.4). The compromise between the two regimes provides better resolution for the surface of soft samples than non-contact regime and less sample modification than the contact regime (DeRose and Leblanc, 1995).

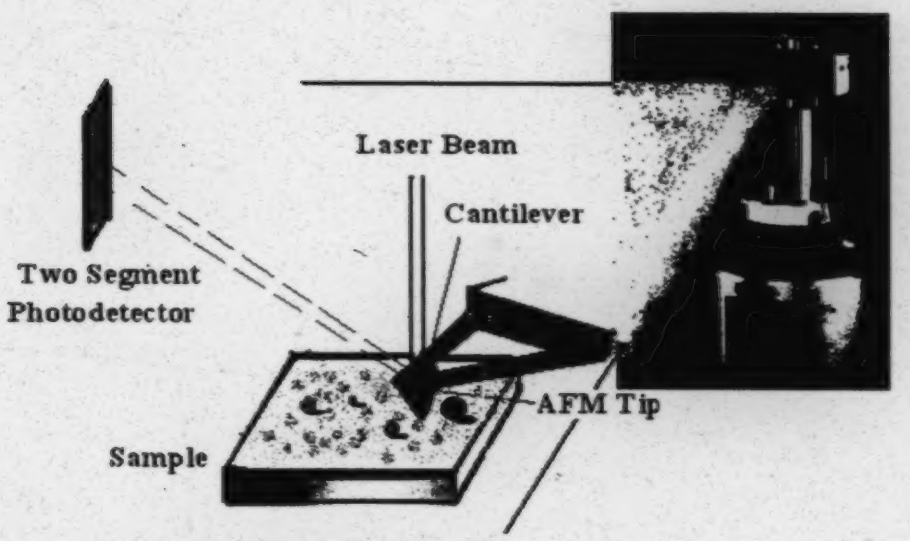


Figure 4.4. A general schematic representation of the AFM system.

4.8. References

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Chapter 5

Preliminary Experimental Studies

Preliminary experiments were concerned with using more than one spreading solvent, different amounts of prepared solutions, different evaporation time of the spreading solvent, and different methods for the preparation of an interfacial film.

Using chloroform as an alternative spreading solvent for bitumen resulted in isotherms nearly identical to the isotherm obtained in case of dissolving bitumen in toluene.

Interfacial pressure-area isotherms were measured for bitumen films created by spreading different volumes of bitumen-in-toluene solutions. In this experiment, starting from 300 μL of the solution (1mg/mL), further increase in the solution volume did not cause any changes in the recorded isotherms. When different evaporation periods of the spreading solvent were used, 10 minutes was found to be sufficient for evaporation time.

The approximate thickness of bitumen monolayer deposited from the air/water interface was estimated to be ~2nm.

Once the time for complete evaporation of a volatile solvent had been chosen, three different trials were performed using different methods to prepare an interfacial bitumen film at the toluene/water interface. It was demonstrated by the reproducibility and consistency of these three experimental results that subjecting the monolayer to air did not appear to be critical. All of the recorded isotherms displayed were similar.

5.1. Using Toluene and Chloroform as the Spreading Solvents for Bitumen

In Langmuir trough experiments, amphiphilic molecules are spread on a water surface. It is common to use a volatile, water-insoluble spreading solvent for substances which do not spread well themselves. The spreading solvent must have sufficient solvency power and have the ability to prevent aggregation. For accuracy of measurements, it is desirable to compare results obtained with more than one spreading solvent (Gaines, 1966).

Initial experiments were performed to ensure the reproducibility of the results for more than one spreading solvent. Two different solvents with similar qualities of spreading molecules were used to spread bitumen onto a water surface. For this purpose, two separate solutions were prepared by dissolving bitumen in toluene and chloroform at a concentration of 1 mg/mL each. Bitumen films were formed after 20 µl of bitumen-in-toluene and bitumen-in-chloroform solutions were separately spread on the water surface. Compression of these films showed no significant difference in the pressure-area isotherms. The comparison of the isotherms recorded while compressing the above mentioned films is shown in Figure 5.1. The difference between these two isotherms was within the experimental error. The results were consistent as expected, presumably due to the high solubility of bitumen in toluene and chloroform, and high volatility of these two solvents.

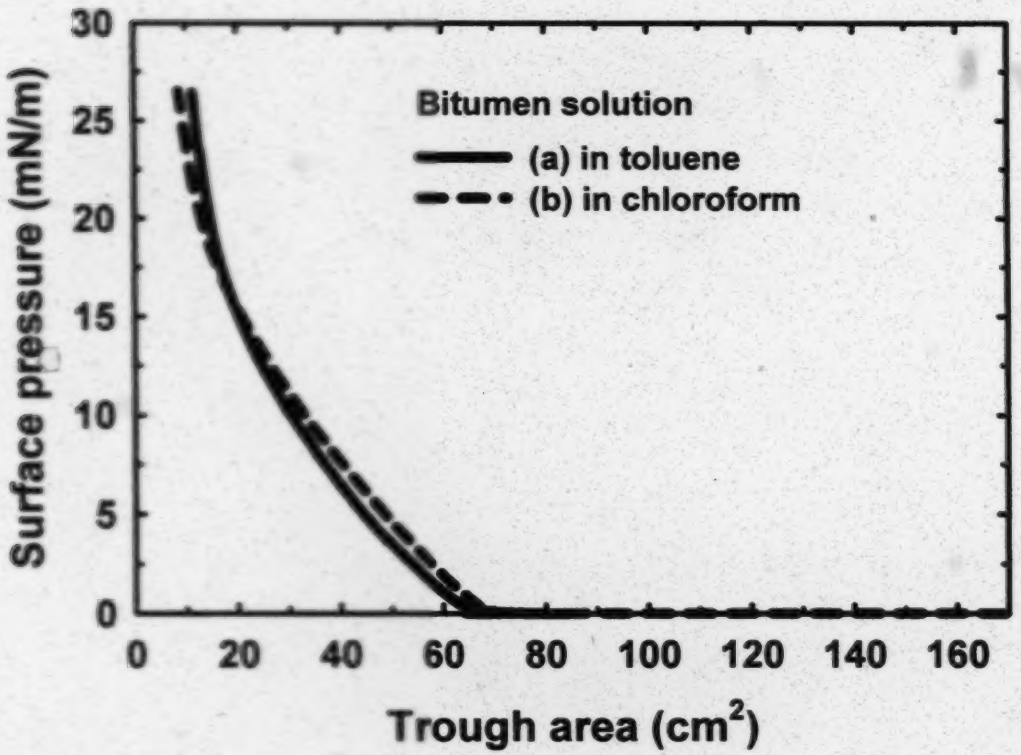

Figure 5.1. Surface pressure-area (π-A) isotherms of bitumen monolayers at air/water interface. 20 µl of bitumen (a) in toluene and (b) in chloroform, 1mg/mL bitumen concentrations.

5.2. Volume of the Spreading Solution

Four different trials were performed with bitumen films at toluene/water interface. In each trial, a different volume of a 1mg/mL bitumen-in-toluene solution was spread on the water surface and covered with 100 mL of toluene top phase.

Figure 5.2 shows a comparison between the interfacial pressure-area (π-A) isotherms for bitumen films formed after spreading different volume of the bitumen-in-

toluene solution. The isotherm obtained for 100 μL of solution is lower than other recorded isotherms. For a given trough area, the interfacial pressure is lower. Starting from 300 μL, further increase in the volume of the bitumen solution did not affect the pressure- area isotherms. Increasing the spreading volumes resulted in the adsorption of the same amount of interfacially active materials, as evident from the identical isotherms recorded for 300, 600, and 1000 μL of the solution. This finding confirms that use of 100 μL 1 mg/mL bitumen solution is insufficient to cover whole trough area by surface active molecules.

When 300, 600, or 1000 μL of the bitumen-in-toluene solution was spread onto water, a multilayer bitumen film was formed at air/water interface upon the evaporation of toluene spreading solvent. However, upon the addition of the 100 mL of a bulk toluene phase, any excess bitumen material migrated to the bulk toluene phase, leaving behind a single adsorbed layer at toluene/water interface.

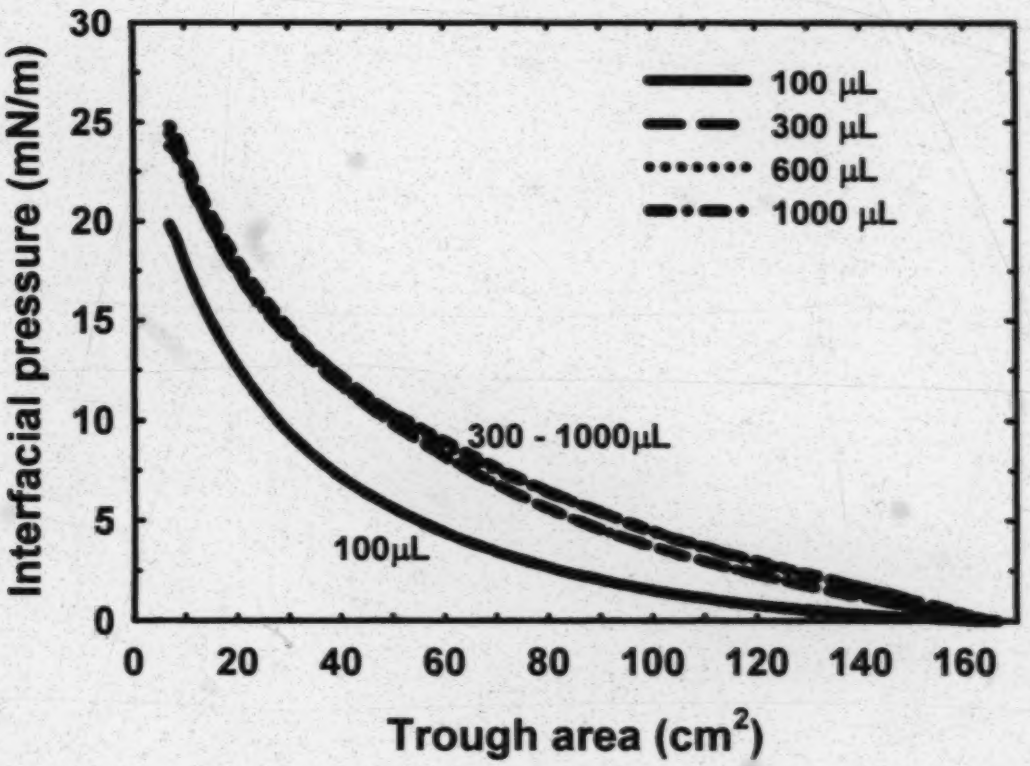

Figure 5.2. Interfacial pressure-area (π-A) isotherms of bitumen films at toluene/water interface by applying different volumes (100, 300, 600, and 1000 µL) of spreading solution (bitumen-in-toluene solution, 1mg/mL)

5.3. Evaporation Period of the Spreading Solvent

The next set of experiments was performed to determine the sufficient waiting time for complete evaporation of the spreading solvent (toluene).

First, experiments were conducted for air/water interface. A bitumen monolayer was formed by spreading 20 µL of 1mg/mL bitumen-in-toluene solution. After the solution was spread onto water surface, different time intervals were allowed for spreading solvent to evaporate. The isotherms were recorded after 5, 10 and 30 minutes of solvent

evaporation. Figure 5.3 shows that five minutes was not sufficient for complete solvent evaporation since there was a significant change in the isotherms recorded after 10 minutes of solvent evaporation. However, after 10 minutes, the increase in the solvent evaporation time did not play any critical role. The isotherms recorded after 10 and 30 minutes closely match each other (Figure 5.3).

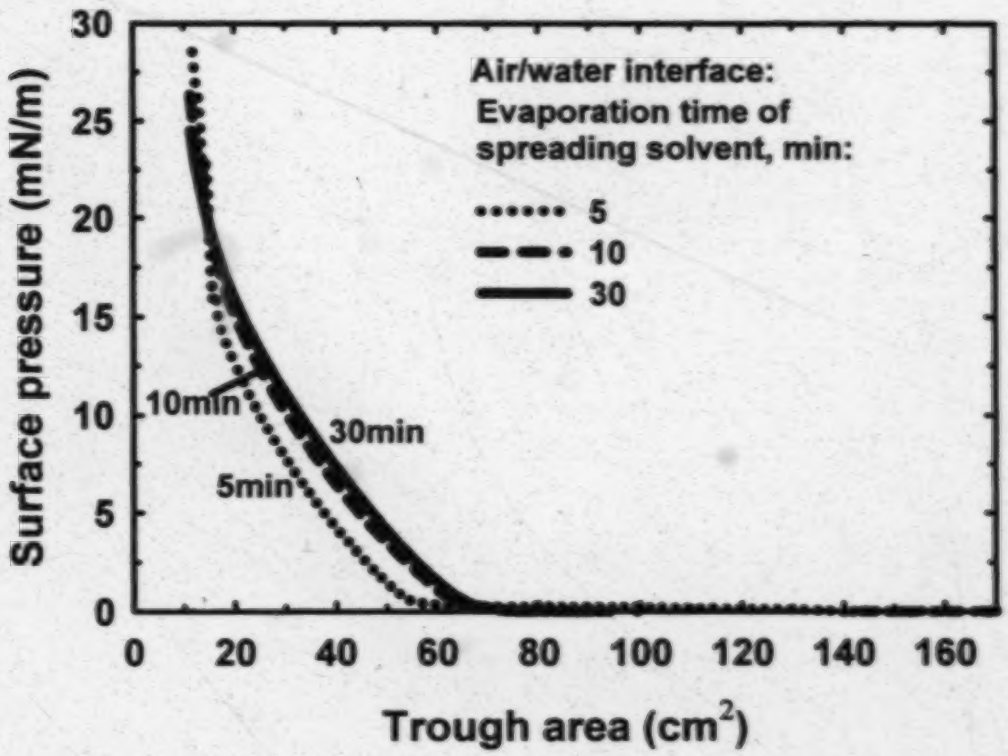

Figure 5.3. Surface pressure-area (π-A) isotherms of bitumen monolayers at the air/water interface (20 μL of bitumen in toluene solution, 1mg/mL). Time for spreading solvent evaporation: 5, 10 and 30 min.

Similar experiments were performed for the toluene/water interface. A 100 μL of bitumen in toluene solution was spread onto the water surface. Intervals of different

duration were chosen prior to covering the prepared monolayer by the toluene top phase. When the bitumen monolayer was covered by toluene immediately after spreading, the resulting isotherm showed less material at the interface, curve (a) in Figure 5.4. The monolayer forming molecules of bitumen remained in a highly diluted film composed largely of solvent. Concentration of the studied material increases with solvent evaporation, resulting in a greater surface pressure if sufficient time is allowed. Asphaltene film exhibited similar behaviour at the toluene-water interface when compressions were conducted after 0 and 10 minutes of solvent evaporation (Zhang et al., 2005).

The concentration of surface active material increased with increasing solvent evaporation time. Figure 5.4 shows that nearly identical isotherms were obtained for 100 μL of bitumen-in-toluene solution after 10 and 90 minutes of solvent evaporation. Any further prolonged evaporation time (up to 90 minutes) than 10 minutes did not cause any shift in the recorded isotherms.

Through a series of experiments, it was found that starting from 10 minutes of evaporation, there was no further increase in the concentration of non-volatile components in bitumen monolayers at air/water or toluene/water interfaces. It can be concluded that for the purpose of monolayer preparation, a period of 10 minutes was sufficient for complete evaporation of the spreading solvent (toluene). As a result, 10 minutes was chosen as the waiting period throughout our experiments for evaporation of the spreading solvent.

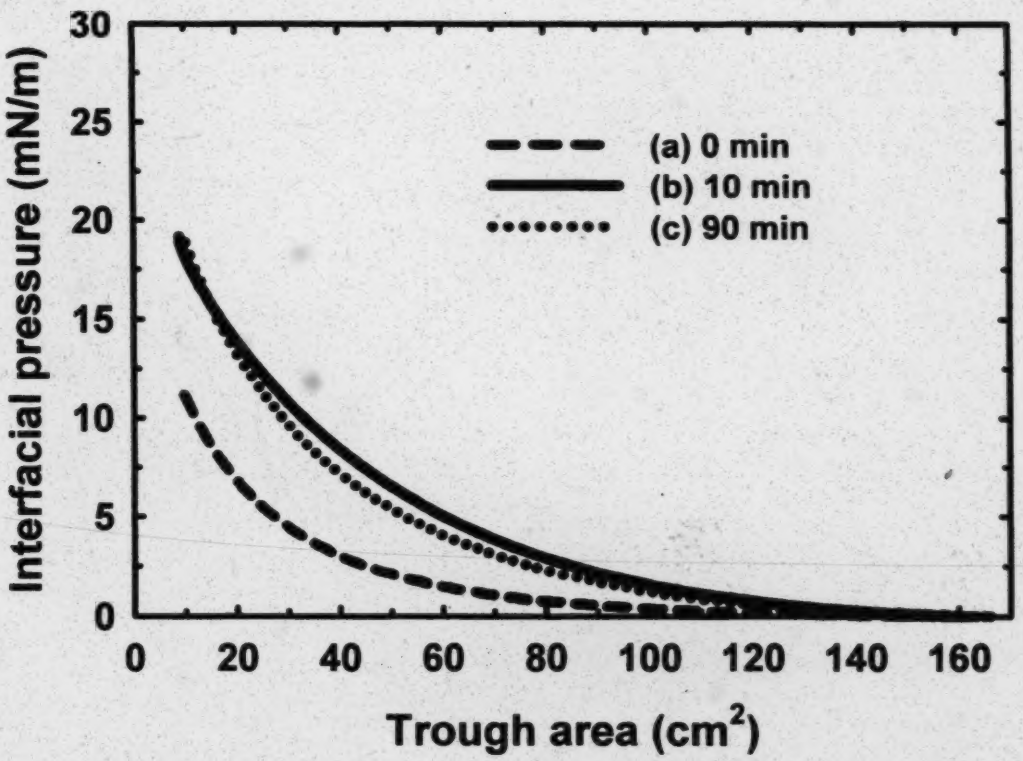

Figure 5.4. Interfacial pressure-area (π-A) isotherms of bitumen monolayers (100 μL of bitumen in toluene solution 1mg/mL) at the toluene/water interface at different evaporation periods of the spreading solvent: (a) 0, (b) 10, (c) 90 minutes.

5.4. Analysis of the Bitumen LB Film

A section of the AFM image (10x10μm) obtained from LB bitumen film deposited from the air/water interface is shown in Figure 5.5. The bitumen film was prepared at air/water interface by spreading 20 μL of bitumen-in-toluene solution. The LB film was deposited from the air/water interface using the method described previously. The image shows a non-uniform character of the surface. The domains of constant brightness with dimensions in the micron range are divided by clearly defined

borders. The image revealed larger aggregate structures than images for the LB bitumen films deposited from solvent/water interfaces (shown in the following sections). The film was damaged during the film transfer, creating an ideal case for thickness evaluation of the deposited bitumen films. A small portion of the substrate left uncovered (dark area in Figure 5.5). The film thickness was evaluated by measuring the vertical distance between uncovered substrate (silicon wafer) surface and the averaged LB film surface. The medium height was about 2 nm, which made us to believe that the transferred film was monolayer.

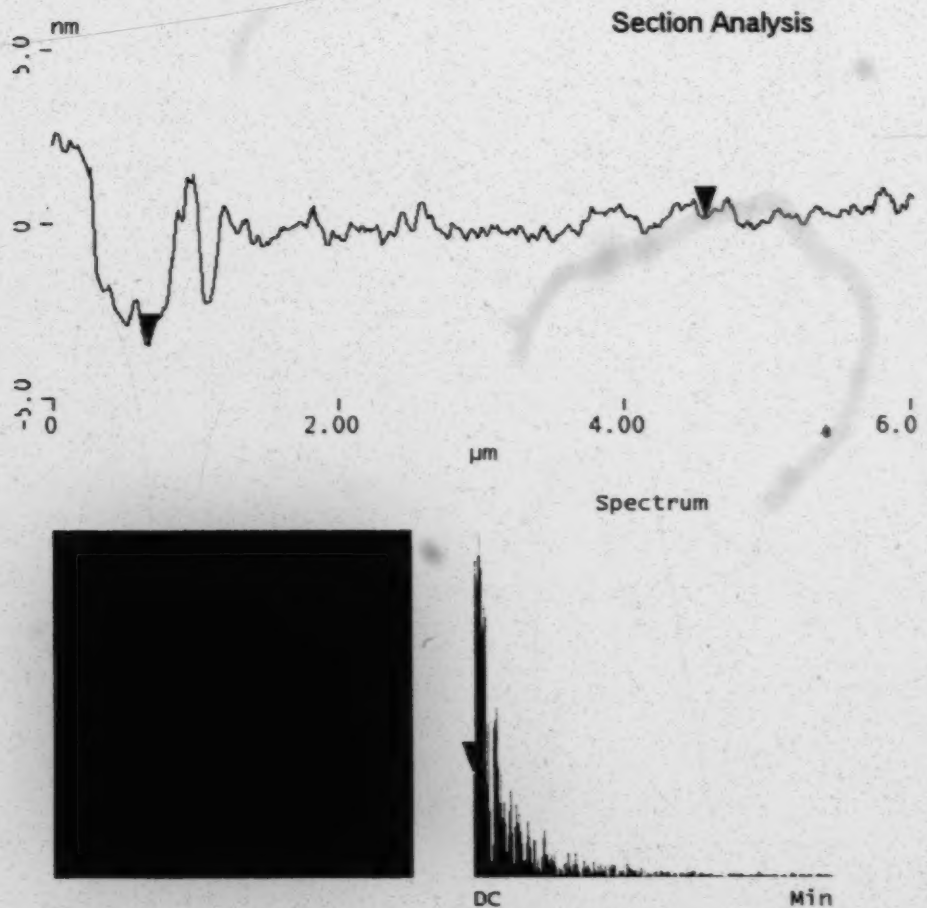

Figure 5.5. Section analysis of the LB bitumen film deposited from the air/water interface.

5.5. Different Methods of Preparation a Bitumen Film at Toluene/Water Interface

One method of preparing an interfacial film is to spread the material of interest in a solvent onto a water surface, and then, cover the created film with a layer of toluene as the top phase after the spreading solvent evaporation. In this method, described earlier and used throughout our experiments, after 10 minutes of the spreading solvent evaporation, the film was covered by 100 mL of toluene top phase and left for 30 minutes prior to compression. Isotherm (a) of Figure 5.6 was recorded for the bitumen film prepared by spreading 100 μL of 1mg/mL bitumen-in-toluene solution onto water. For isotherm (b), the time after adding 100 mL of toluene was increased up to 40 minutes. Curves (a) and (b) are nearly identical. (Increasing the waiting time up to 60 minutes did not affect the result either.) In the experiments described above, the environment for the hydrophobic parts of the surface active molecules was altered when the spreading solvent was removed by evaporation. An alternative method to prepare an interfacial film is to introduce the solution containing bitumen (100 μL of bitumen-in-toluene solution, 1mg/mL) into the top solvent phase with a microsyringe. The results obtained with this procedure are shown as isotherm (c) in Figure 5.6. In case (d), bitumen was diluted in the 100 mL of toluene to be used as the top phase at a concentration of 0.001 mg/mL to avoid the exposure of a bitumen film to air. The interfacial components slowly adsorbed from the solvent top phase, forming a film at toluene/water interface.

The experimental results obtained with various film preparation procedures did not show substantial variation of the prepared bitumen films.

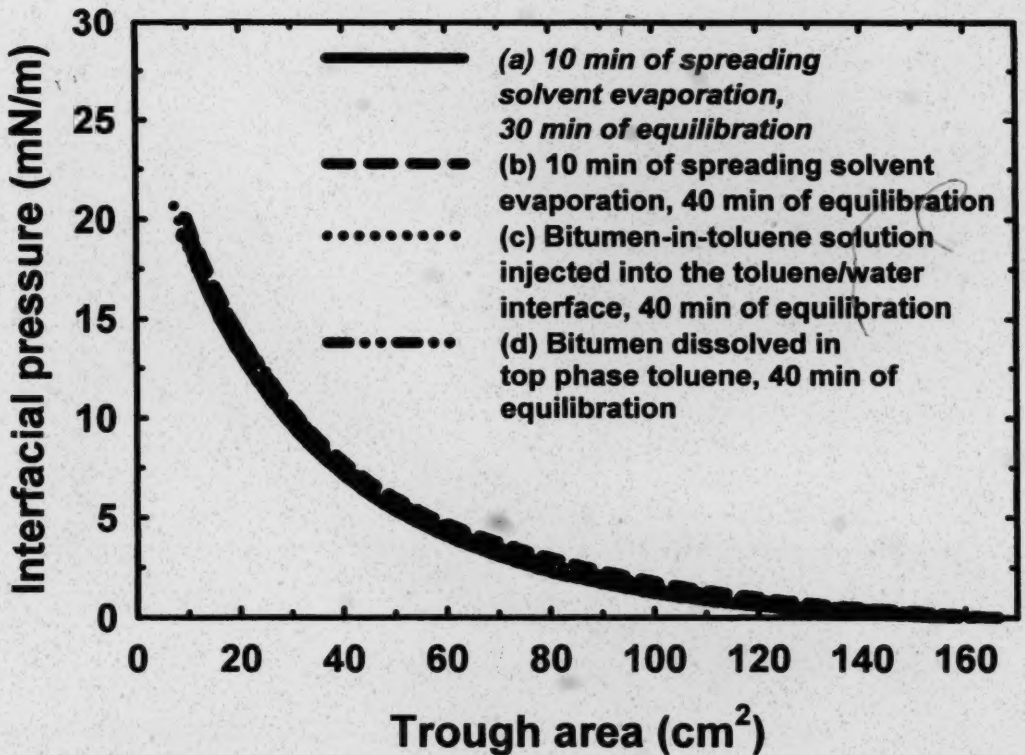

Figure 5.6. Comparison of (π-A) isotherms recorded for adsorbed and spread bitumen monolayers at toluene/water interface. (a) Bitumen monolayer prepared by spreading 100 µL of 1mg/mL bitumen-in-toluene solution. After 10 minutes of the spreading solvent evaporation, the film was covered by 100 mL of toluene top phase and left for 30 minutes prior to compression. (b) Spread bitumen film prepared as described in (a), 40 minutes of equilibration instead of 30. (c) 100 mL of toluene was placed onto water, 100 µL of 1mg/mL bitumen-in-toluene solution was injected into the interface, 40 minutes of equilibration. (d) Adsorbed bitumen film from 100 ml of bitumen-in-toluene solution at concentration of 0.001 mg/mL placed onto water, 40 minutes of equilibration.

5.6. References

(1) Gaines, G. L., *Insoluble Monolayers at Liquid-Gas Interfaces,* New York, Interscience Publishers, 1966.

(2) Zhang, L. Y., Lopetinsky, R., Xu, Z., Masliyah, J. H. Asphaltene Monolayers at a Toluene/Water Interface. *Energy & Fuels*. **2005**, *19*, 1330 – 1336.

Chapter 6

Composition of Oil Phase Effect on the Bitumen Film Compressibility

The chapter discusses the effect of aromaticity of the solvent phase and acetone addition to toluene top phase on the bitumen film compressibility. The aromaticity of the solvent top phase was varied by controlling heptane to toluene ratio. Heptane as a solvent phase caused reduction of the molecular solubility of bitumen. The experimental results showed that the bitumen film becomes more compressible with increasing content of toluene thereby increasing aromaticity of the solvent top phase. Similarly, when acetone was added to toluene, the bitumen and asphaltene films became more compressible.

6.1. Effect of Aromaticity of Oil Phase

The aromaticity of the solvent top phase was varied by controlling heptane/ toluene ratio. To this end, 100 μL of bitumen-in-toluene solution was placed first on the surface of water subphase, after toluene evaporation, heptane, toluene or heptol (a mixture of heptane and toluene at a heptane/toluene volume ratio of 50/50 or 80/20) was placed on the top and used as the organic top phase. Figure 6.1 shows the π-A isotherms for bitumen monolayers recorded at toluene/water, heptane/water and heptol/water interfaces. The results of Figure 6.1 show that the highest attainable interfacial pressure increases with increasing heptane content in the top phase. The bitumen film becomes more compressible with increasing content of toluene thereby increasing aromaticity of the top phase solvent. The highest compressibility of bitumen monolayer is exhibited at

the toluene/water interface. The results of Figure 6.1 indicate that the hydrocarbon side chains of bitumen molecules have different conformations when they are embedded in different solvents with varying aromaticity.

The behavior of bitumen monolayers as observed in Figure 6. 1 is similar to the behaviour of asphaltene monolayers at heptol/water interfaces, as reported by Zhang et al. (2005) and McLean et al. (1998). According to Zhang et al. (2005), asphaltene films become more flexible as heptane content in heptol decreases. With increasing aromaticity of the solvent phase, both the highest attainable interfacial pressure and the rigidity of an asphaltene film decrease. We also observed these trends for bitumen films as discussed above. A correlation was established by McLean et al. (1998) between the stability of emulsions stabilized by asphaltenes and the solvent aromaticity. They concluded that asphaltenes become less surface active with increasing aromaticity of the solvent.

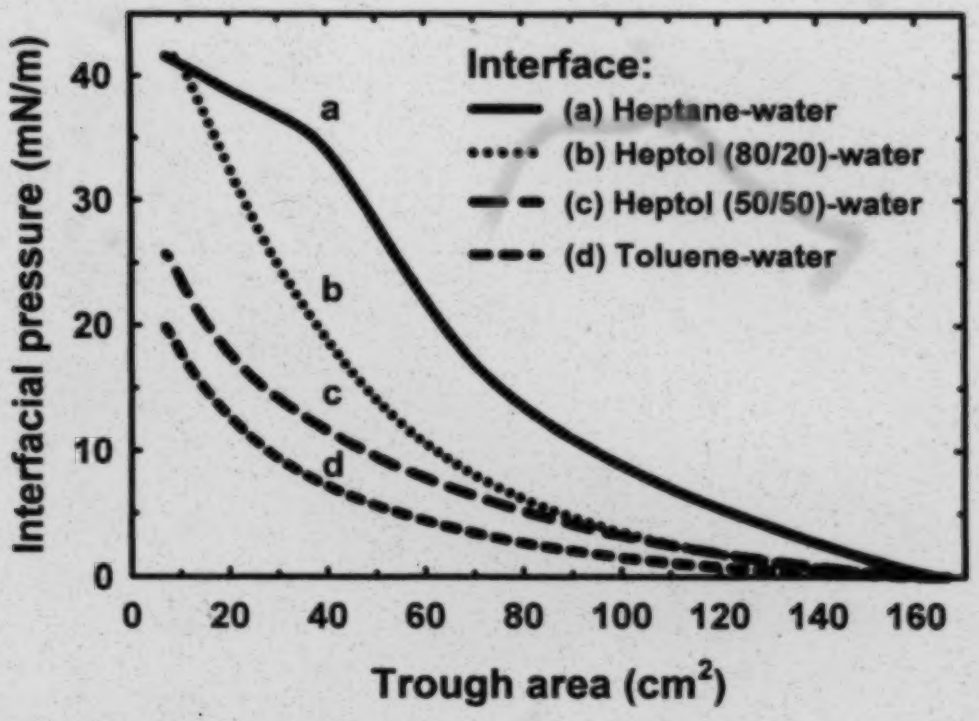

Figure 6.1. Interfacial pressure-area (π-A) isotherms of bitumen monolayers at various oil/water interfaces: (a). Heptane/water interface; (b). Heptol (80:20)/water interface; (c). Heptol (50:50)/water interface; and (d). Toluene/water interface.

For further comparison, AFM imaging of LB bitumen films deposited from toluene/water and heptane/water interfaces was performed. The AFM topographic images obtained in tapping mode under the same magnification are presented in Figure 6.2. The LB bitumen films were deposited at a constant interfacial pressure of 10 mN/m. As expected, bitumen films deposited from toluene/water interface in (a) and from heptane/water interface in (b) differ in morphological characteristics. The brighter areas in both images of Figure 6.2 represent molecular aggregates. In image (b), molecular

aggregates are larger than in image (a). Clearly, toluene can be chosen as a solvent for bitumen to minimize the size of aggregates created by the interfacial active components.

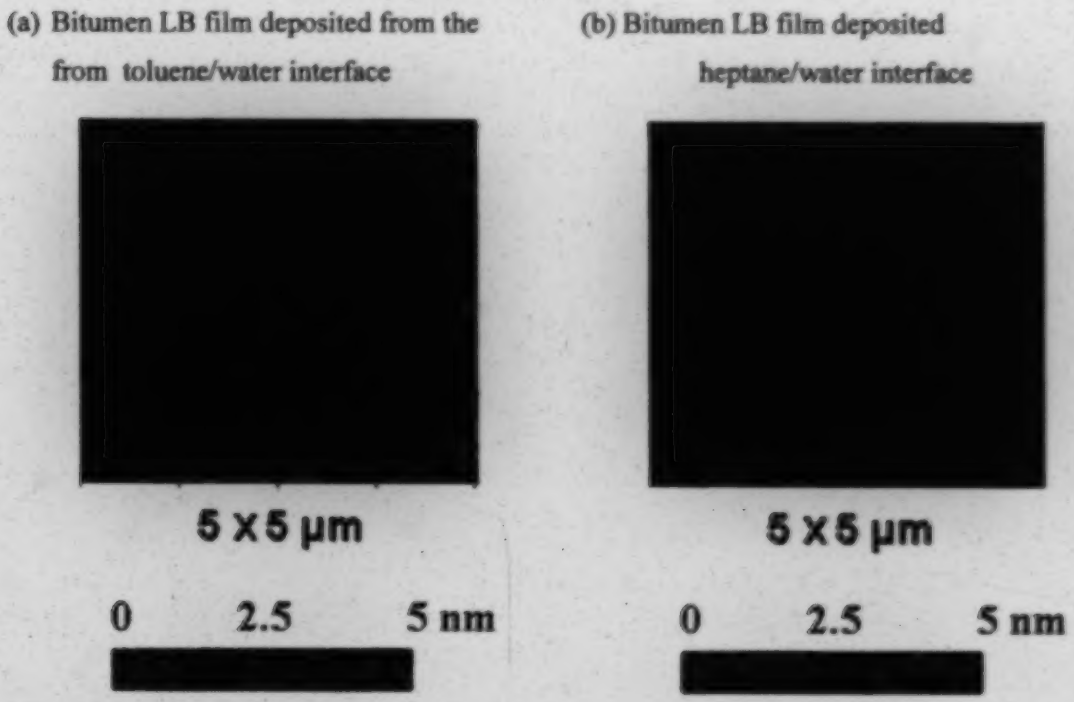
(a) Bitumen LB film deposited from the from toluene/water interface
(b) Bitumen LB film deposited heptane/water interface
5 X 5 µm
5 X 5 µm
0 2.5 5 nm
0 2.5 5 nm

Figure 6.2. Tapping mode AFM topographic images of bitumen LB films deposited from (a) toluene/water interface, TR=1.2, and (b) heptane/water interface TR=1.8.

6.2. Effect of Acetone Addition as a Co-Solvent

Zhang et al. (2005) conducted experiments evaluating the effect of addition of 2-propanol into the bulk toluene top phase on interfacial behaviour of asphaltenes. The results obtained from the experiments utilizing a Langmuir trough and AFM showed that 2-propanol molecules most likely penetrated into the asphaltene monolayer, weakening the asphaltene molecular interactions.

Similar to isopropyl alcohol, acetone can be mixed with toluene. Its miscibility with numerous solvents (one of which is toluene) permits its use as a co-solvent thereby changing the quality of solvent. Acetone is known to dissolve the lighter constituents of asphaltenes and bitumen (Rembler, 1923). Mixed solvents, such as acetone/hydrocarbon mixture can give sufficient solubility for some materials while at the same time not causing any water-solubility problems (Gaines, 1966).

In this set of experiments, the compressibility of bitumen and asphaltene films was evaluated at a toluene and acetone mixture/water interface. The solution of interest was spread at water surface. Then, after spreading solvent evaporation, 100 mL of toluene and acetone mixture was added as a top phase. Asphaltene and bitumen films were compressed at 1:1 toluene to acetone mixture/water interface. Figures 6.3 and 6.4 show the resulting isotherms, compared to isotherms recorded on compression of asphaltene and bitumen films at toluene/water interfaces (a). The maximum attainable interfacial pressure for bitumen and asphaltene films at toluene/water interface was ~20 mN/m. The maximum interfacial pressure values for films created by spreading the same amount of bitumen and asphaltene solutions as for toluene/water interface dropped from 20 mN/m to ~ 4mN/m for asphaltene, and to ~ 1mN/m for bitumen films. It seems that a combination of acetone and toluene enhanced solubility of the asphaltene and bitumen interfacial films.

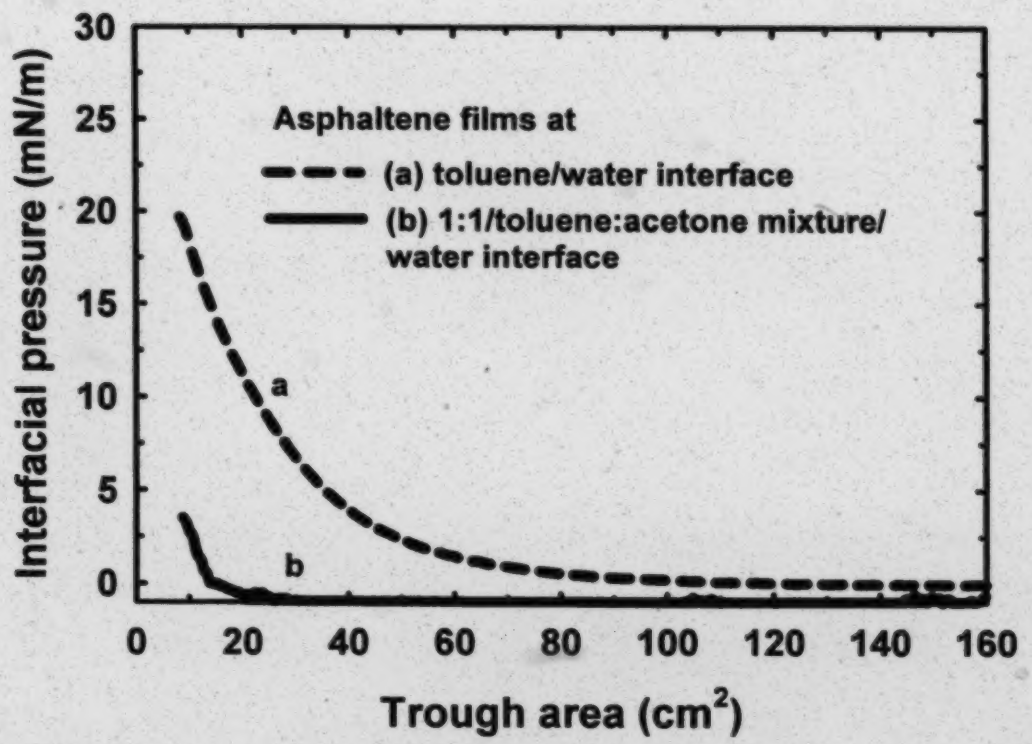

Figure 6.3. Interfacial pressure-area (π-A) isotherm of asphaltene films at (a) toluene/water interface and (b) 1:1/toluene:acetone mixture/water interface.

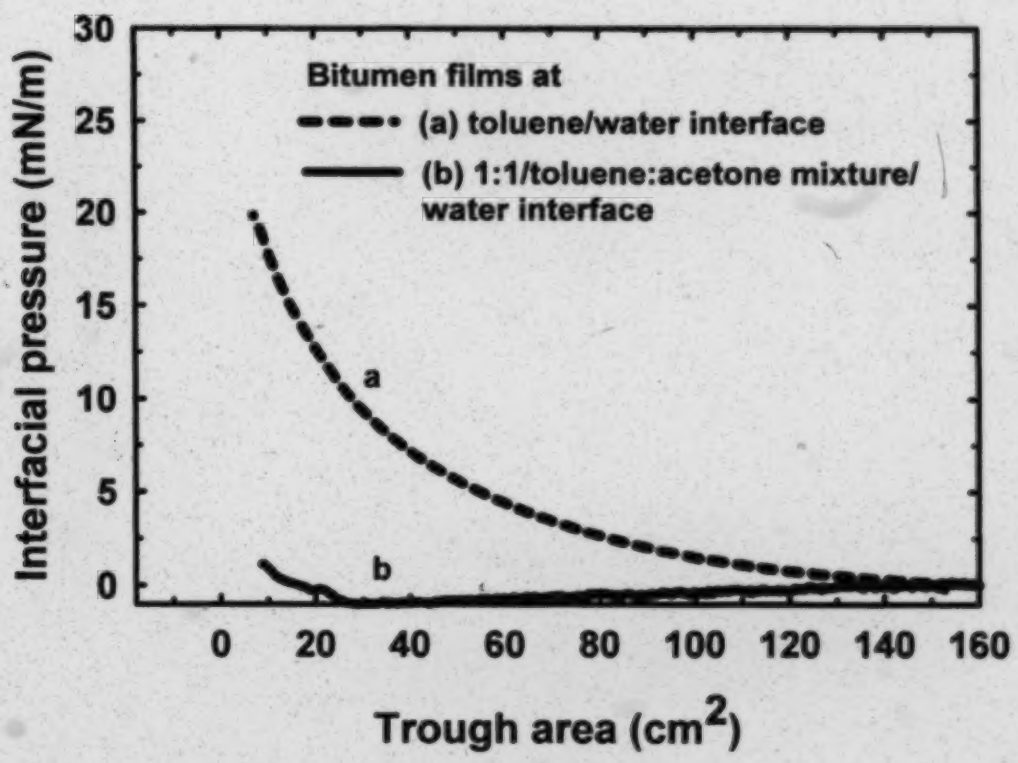

Figure 6.4. Interfacial pressure-area (π-A) isotherm of bitumen films at (a) toluene/water interface and (b) 1:1/toluene:acetone /water interface.

6.3. Effect of Composition of Oil Phase on Bitumen Film Compressibility: Summary

In the aromatic solvent method of froth treatment utilized by Syncrude, naphtha is used as an aromatic solvent. A mixture of heptane and toluene (heptol) used in the above discussed experiments better represents the solvent properties of naphtha with respect to asphaltenes solubility than toluene alone. However, the experimental results showed that a bitumen film becomes more compressible at the toluene/water interface. The highest bitumen film compressibility was achieved when acetone was added to

toluene. Addition of a polar co-solvent, such as acetone to toluene caused solubility enhancement due to the chemical interaction between the solute and the co-solvent. These experimental results indicate the importance on the selection of the co-solvent.

6.4. References

(1) Zhang, L.Y., Xu, Z., Masliyah, J. H. Characterization of Adsorbed Athabasca Asphaltene Films at Solvent-Water Interfaces Using a Langmuir Interfacial Trough. *Ind. Eng. Chem. Res.* **2005**, *44*, 1160 – 1174.

(2) McLean, J. D., Spiecker, P. M., Sullivan, A. P., Kilpatrick, P. K. The Role of Petroleum Asphaltenes in the Stabilization of Water-in-Oil Emulsions. In *Structure and Dynamic of Asphalenes*, Sheu, E., and Mullins, O., Eds.; Plenum: New York, **1998**; 377-422.

(3) Zhang, L. Y., Lopetinsky, R., Xu, Z., Masliyah, J. H. Asphaltene Monolayers at a Toluene/Water Interface. *Energy & Fuels*. **2005**, *19*, 1330-1336.

(4) Rembler, R. F. The Solvent Properties of Acetone. *Ind. Eng. Chem.* **1923**, 717.

(5) Gaines, G. L., *Insoluble monolayers at liquid-gas interfaces*, New York, Interscience Publishers, **1966**.

Chapter 7

Experimental Study of the Adsorption Reversibility

This chapter deals with the experimental study of adsorption reversibility or ability of an interfacial material of bitumen, maltenes and asphaltenes to leave the interface upon replacement of the initial top phase solvent with a fresh one.

If the interfacial material is able to leave an interface, its presence can be revealed in either of the bulk phases. The solvent top phase and water subphase were checked for the presence of desorbed species by covering the recovered liquid phase with a fresh phase either sub-water or top-toluene.

To make the experimental conditions closer to industrial conditions, a series of experiments with bitumen, asphaltene and maltene films was conducted where recycle Aurora plant process water was used as the aqueous subphase. The mass of the extracted asphaltene was approximately 15 % of the mass of bitumen used in this study. To reflect the actual content of asphaltene and maltene in bitumen, the volumes of bitumen, asphaltenes and maltenes solutions in toluene (at 1g/L concentration) spread on aqueous subphase were as follows: 100 μl for bitumen solution, 15 μl for asphaltenes solution and 85 μl for maltenes solution. These spreading volumes were chosen to ensure an equitable comparison among bitumen, asphaltene and maltene films.

7.1. π–A Isotherms of Bitumen, Asphaltene and Maltene Films at Toluene/Water and Heptane/Water Interfaces.

Figure 7.1 shows the π-A isotherms for bitumen, asphaltene, and maltene films at a toluene/water interface. The isotherms for these films at the heptane/water interface are shown in Figure 7.2. It is evident from Figures 7.1 and 7.2 that the highest attainable interfacial pressures for the bitumen and the asphaltene films are about the same, ~20 mN/m at the toluene/water interface and ~ 40 mN/m at the heptane/water interface. The values of the highest attainable interfacial pressure for bitumen and asphaltene films are much higher than those for the maltene films for both toluene/water and heptane/water interfaces. Figures 7.1 and 7.2 demonstrate that a maltene film is more compressible than either bitumen or an asphaltene film. At a toluene/water interface, the results in Figure 7.1 show that the interfacial pressure-area isotherm of a bitumen film exhibits a higher interfacial pressure reading at a given trough area for $\pi \leq 12.5$ mN/m than that of an asphaltene film. This behaviour is due to the presence of additional interfacial active molecules, such as resins, in bitumen that are absent in asphaltene. These additional interfacial active materials contribute to the observed higher interfacial pressure values. At a heptane/water interface, Figure 7.2 shows the pressure-area curves recorded upon compression of the bitumen film lie above that of the asphaltene film for a given trough area. Furthermore, the pressure difference of these two isotherms at a given trough area is larger for $\pi \leq 15$ mN/m. However, this pressure difference decreased to almost a constant value for $15 < \pi < 35$ mN/m, suggesting migration of resins to the heptane bulk phase. Results of using the collected heptane bulk phase placed on a fresh water surface

(Figure 7.3, curve (b)) showed a considerable interfacial pressure reading upon compression, indicating that the collected heptane contains interfacial active materials. A similar isotherm, isotherm (a) was recorded upon compression of interface created by placing the recovered heptane top phase from maltene film onto the water subphase. Because resins are soluble in heptane, we can conclude that some resins migrated from the heptane/water interface into the bulk heptane phase. The isotherm (c) was obtained using heptane top phase collected from asphaltene film experiment. It did not reveal the presence of detectable asphaltene in the recovered heptane top phase.

These findings indicate the presence of additional interfacial materials in the bitumen film. In general, the trend observed for bitumen, asphaltene, and maltene films at the heptane/water interface in Figure 7.2 is consistent with that observed for these films at the toluene/water interface in Figure 7.1.

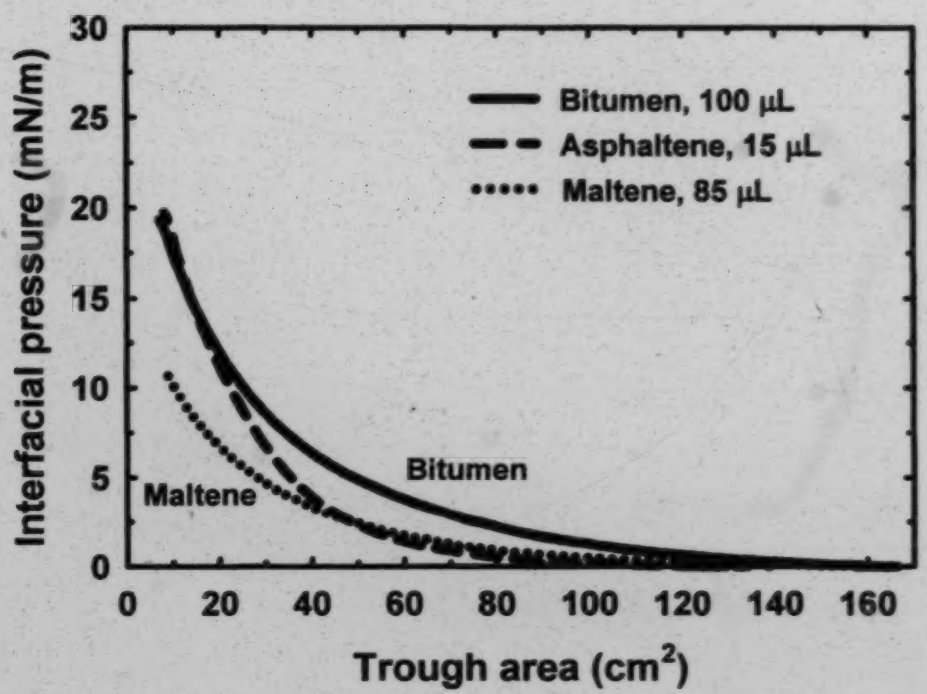

Figure 7.1. Comparison of interfacial pressure-area (π -A) isotherms of bitumen, asphaltene, and maltene monolayers at toluene/water interface.

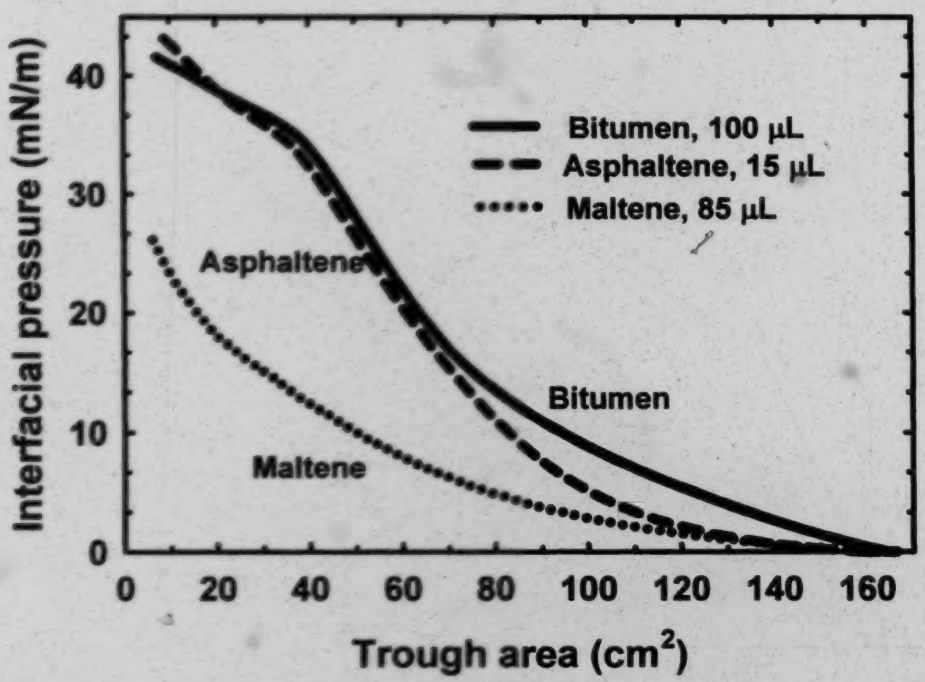

Figure 7.2. Comparison of interfacial pressure-area (π -A) isotherms of bitumen, asphaltene, and maltene monolayers at the heptane/water interface

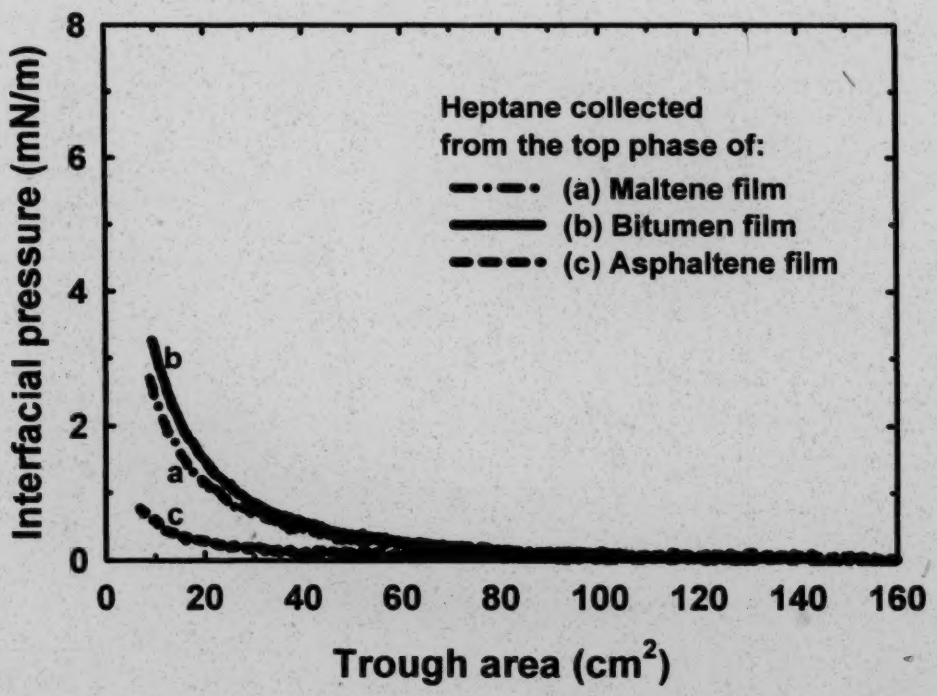

Figure 7.3. Interfacial pressure-area (π-A) isotherms using heptane collected from the top phase from (a) a maltene film, (b) a bitumen film, (c) an asphaltene film.

Figure 7.4 shows a comparison of topographic images of asphaltene, bitumen, and maltene LB films deposited from the toluene/water interface at 10 mN/m. The images for these LB films, deposited onto hydrophilic silicon wafers, were obtained using tapping mode in air at room temperature. The AFM image of the bitumen LB film shows discrete domains occupying most of the surface. For the LB film of asphaltene, the presence of well defined molecular aggregates can be noted on the AFM images. For asphaltene and bitumen films, the images reveal more disc-like features than for the maltene film in which one may note more dark (unpopulated) areas.

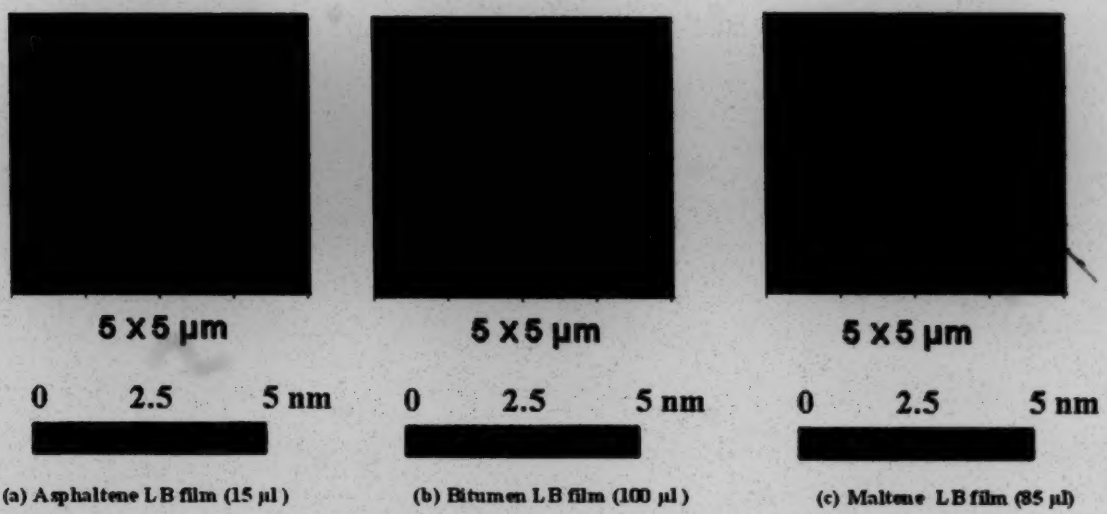

Figure 7.4 . AFM images of asphaltene, bitumen, and maltene LB films deposited from toluene/water interface at 10 mN/m.

7.2. Washing of Bitumen, Asphaltene, and Maltene Films at Toluene/Water Interfaces

In washing experiments, a bitumen film was prepared as described above at the toluene/water interface. After 30 minutes of equilibration, the film at the toluene/water interface was compressed to an interfacial pressure of ~ 20 mN/m and the two barriers were expanded immediately to a full expansion. Then, the toluene top phase was removed and replaced immediately with fresh toluene. After 30 minutes of equilibration, the newly formed toluene/water interface was compressed again to ~ 20 mN/m. This procedure was referred to as washing 1 since the originally prepared bitumen film was washed once with toluene at this stage. The same washing/compressing procedure was repeated several times and those subsequent washings were referred to as washings 2, 3 and so on. Washing experiments for asphaltene and maltene films at a toluene/water

interface were performed following similar procedures used for washing of bitumen films. We also performed washing experiments of a prepared bitumen film at a toluene/water interface by removing the toluene top phase and replacing it immediately with a fresh heptane top phase. After 30 minutes of equilibration, the newly formed heptane/water interface was compressed. Bitumen, maltene and asphaltene films were also prepared at a heptane/water interface using similar procedures as used in preparing bitumen films at a toluene/water interface.

The collected toluene top phase was placed onto a fresh water surface to investigate its interfacial activity. After 30 minutes of equilibration, the newly formed toluene/water interface was compressed to record the interfacial pressure-area (π-A) isotherms.

Figure 7.5 shows the π-A isotherms of a bitumen monolayer, as it was subjected to multiple washings with fresh toluene. A continuous shift toward lower pressure values for a given trough area after the first and second washings is observed in Figure 7.5. After the second washing, there is no visible shift in the pressure area (π-A) isotherms with further washings of the bitumen monolayer. In this case, nearly identical pressure–area (π-A) isotherms for washing numbers 2–6 were observed.

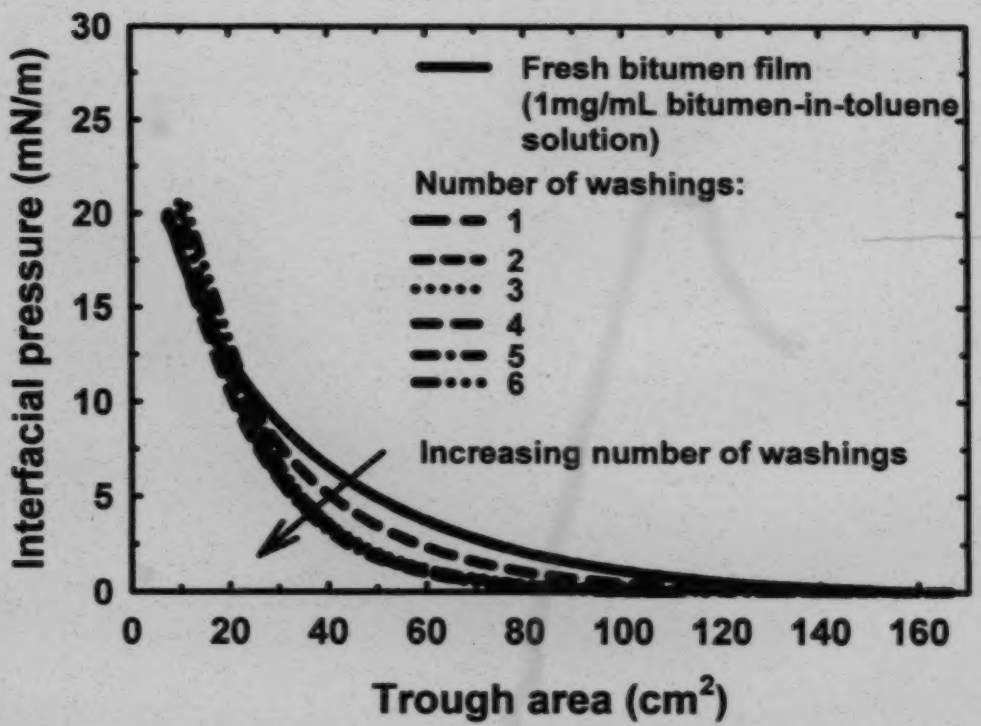

Figure 7.5. Effect of washing with fresh toluene on characteristics of a bitumen monolayer created by spreading 15 μL of 1 mg/mL asphaltene-in-toluene solution.

The surface topography of the LB films of (a) bitumen, (b) bitumen after it was subjected to two washings, and (c) asphaltene is shown in Figure7.6. It can be seen that the structure of the bitumen film which was washed with toluene is altered. There is only a small difference between the features of LB films of asphaltene and washed bitmen film. In Figure 7.6, the images of washed bitumen and asphaltene reveal surfaces more populated with isolated disk-like domains, molecular aggregates. These results can be well correlated with the results of washing experiments, which showed that after two washings with toluene, a bitumen film became very similar to an asphaltene film and exhibited irreversible adsorption as observed for asphaltene films.

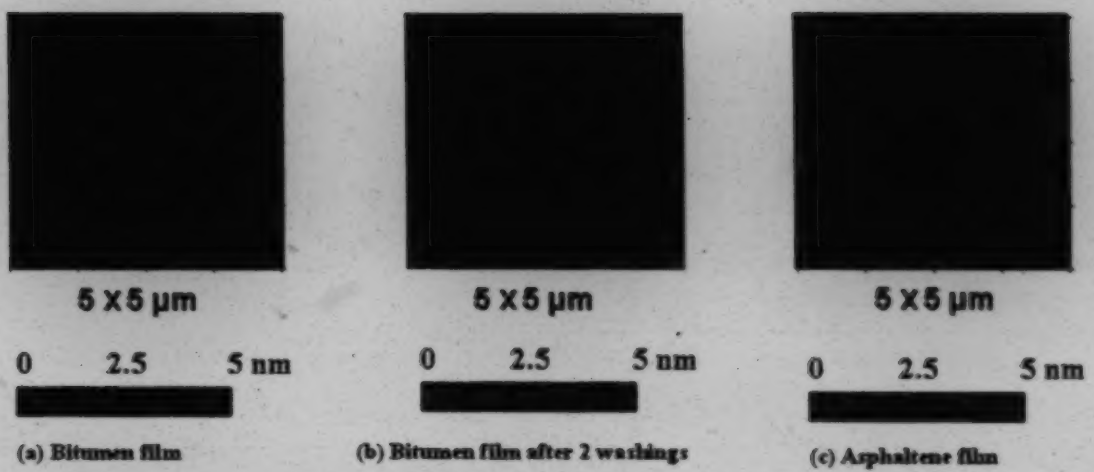

Figure 7.6. AFM images of (a) bitumen, (b) bitumen film after 2 washings, and (c) asphaltene LB films deposited from toluene/water interface at 10 mN/m

Washing experiments similar to those for a bitumen film were conducted for an asphaltene monolayer, and the results are shown in Figure 7.7. In the case of washing an asphaltene film with fresh toluene, the pressure–area (π-A) isotherms obtained after each washing remained nearly identical to that of the original asphaltene monolayer. These results indicate that washing with fresh toluene has a minimal effect on the asphaltene monolayer behaviour at the toluene/water interface. It is clear that the asphaltene material remains at the toluene/water interface and does not migrate from the interface to the washing toluene phase. These observations are in agreement with those reported by Zhang et al. (2005).

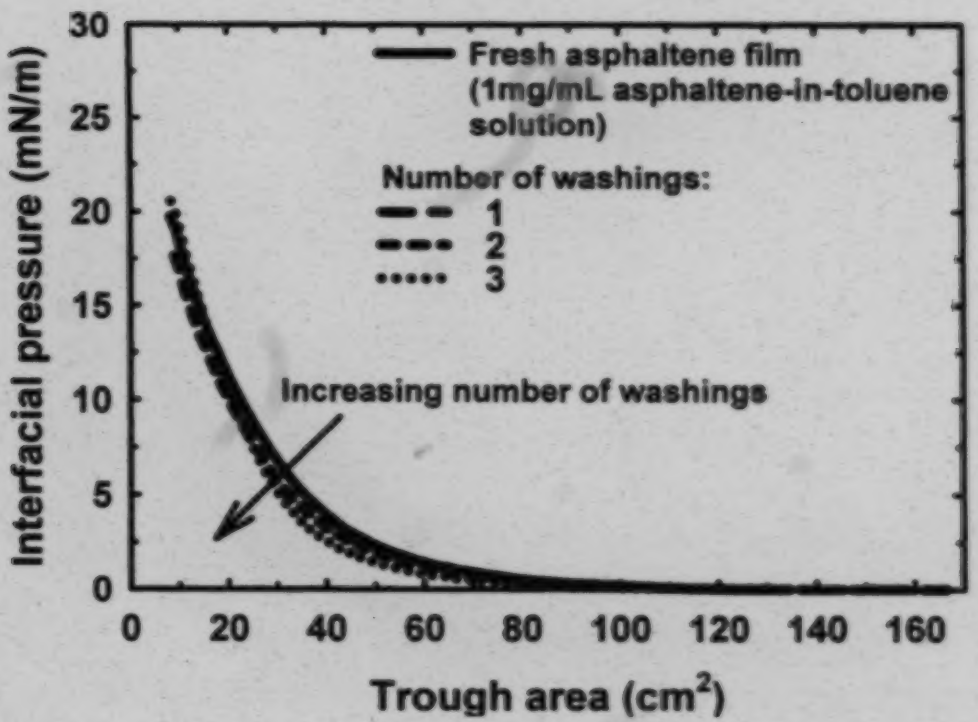

Figure 7.7. Effect of washing with fresh toluene of an asphaltene film created by spreading 15 μL of 1mg/mL asphaltene-in-toluene solution.

Washing experiments were also carried out for the asphaltene film formed by spreading asphaltene-in-toluene solution at a much higher concentration, 10 mg/mL, but same volume of 15 μL. The results of these experiments are shown in Figure 7.8. The isotherms recorded after each washing show that the asphaltene molecules are irreversibly adsorbed for the higher solution concentration as well. There is only a slight shift of the (π-A) isotherms recorded upon consecutive washings. It should be noted that the total amount of asphaltenes used for the case of 15 μL at 1 mg/mL (Figure 7.7) is below a full coverage of the water/toluene interface prior to compression, whereas for

the case of 15 μL at 10 mg/mL (Figure 7.8) it is above full coverage of the interface, where asphaltene multilayers or aggregates are formed. It is for this reason that the pressure–area isotherms presented in Figure 7.8 are higher than those of Figure 7.7. However, their behaviour is similar in the washing experiments.

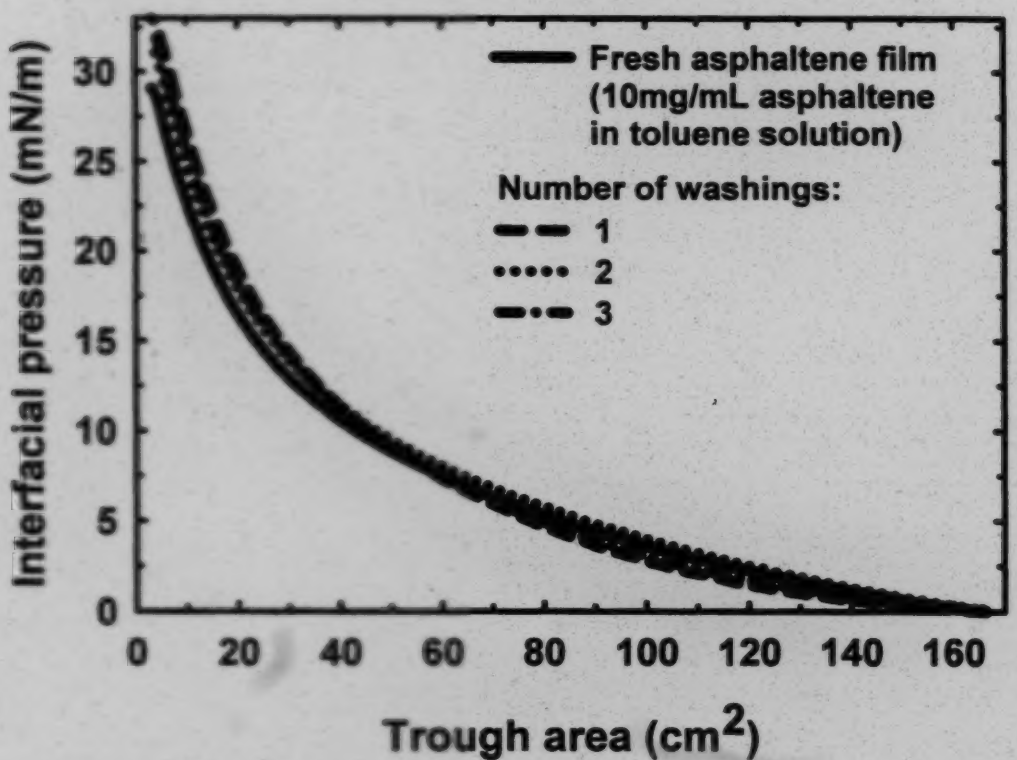

Figure 7.8. Effect of washing with fresh toluene on an asphaltene film created by spreading 15 μL of 10 mg/mL asphaltene-in-toluene solution.

Figure 7.9 shows that when a maltene film was subjected to multiple washings with fresh toluene, the interfacial pressure–area (π-A) isotherms shift continuously toward a smaller trough area for a given pressure as washing progressed. The shift is highest between the isotherm of the original maltene film and that after the first washing. The extension of the continuous shift of (π-A) isotherms decreases with subsequent

washings, indicating that the amount of interfacially active material present at the toluene/water interface decreases by consecutive washings, but to less extent with each washing. This behaviour would indicate that maltenes contain surface-active material that is not irreversibly adsorbed at the interface. However, even after seven washings, there remains some surface active material that most likely is irreversibly adsorbed at the interface. This is not surprising because as maltenes are a solubility class containing molecules that behave like asphaltenes.

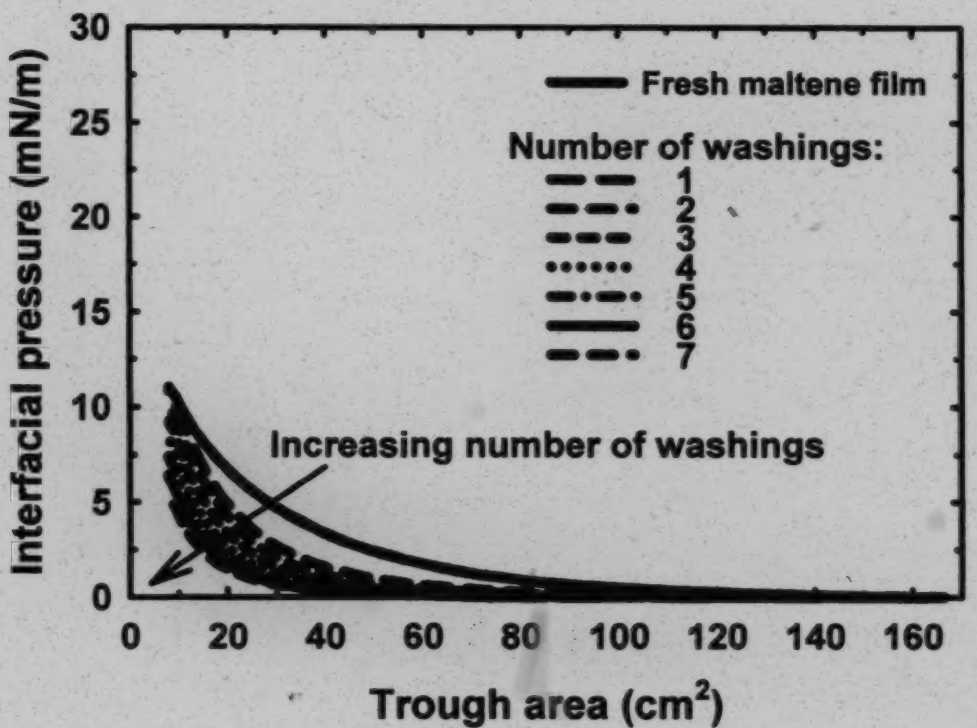

Figure 7.9. Effect of washing with fresh toluene on characteristics of a maltene monolayer.

A washing experiment with heptane was also conducted. Figure 7.10 shows a comparison of the (π-A) isotherms of a bitumen monolayer at the heptane/water interface, curve a; a bitumen film washed once with heptane, curve b; and an original asphaltene monolayer at the heptane/water interface, curve c. In the case of curve b, a bitumen film was initially prepared at the toluene/water interface and the toluene top phase was removed and replaced by heptane. The results in Figure 7.10 show that, after replacement of the toluene top phase by heptane, the (π-A) isotherm of a bitumen film at the heptane/water interface is nearly identical to the isotherm of an asphaltene film at a heptane/water interface. These results further confirm that bitumen films at toluene/water interface are mainly composed of asphaltenes.

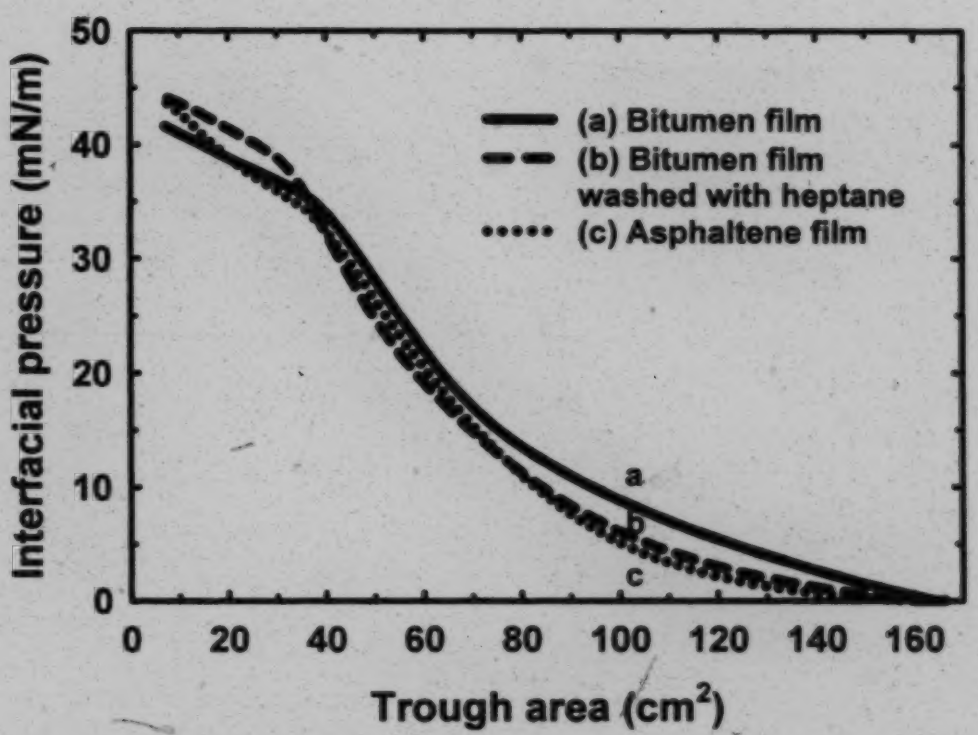

Figure 7.10. Comparison of interfacial pressure-area (π-A) isotherms of: (a). Original bitumen film at the heptane/water interface; (b). A bitumen film was initially prepared at

toluene-water interface. After 30 minutes of equilibration, the toluene was removed and replaced by heptane. After another 30 minutes of equilibration, the bitumen film was compressed at the newly formed heptane/water interface; and (c). Asphaltene film at heptane/water interface.

Experiments were conducted to determine whether any surface active material migrated from the prepared bitumen, asphaltene, and maltene interfacial films to the toluene top phase or the water subphase. After compression of an asphaltene, bitumen, or maltene film at toluene/water interface, the toluene top phase was recovered and placed onto a fresh water surface. After 30 min of equilibration, the newly formed toluene/water interface was compressed, and the results are shown in Figure 7.11. For the case of maltenes, the newly formed toluene/water interface can be compressed up to π~2.4 mN/m, curve (a). For the case of bitumen, the newly formed interface at the collected toluene/freshwater interface can be compressed up to π~2.5 mN/m, a pressure similar to that for the case of maltenes. However, with the collected toluene top phase after two washings of a bitumen film, the interfacial pressure becomes much lower as shown by curve c of Figure 7.11, indicating a marginal amount of surface-active material in the collected toluene. These results indicate that interfacially active materials migrated from the prepared bitumen film to the toluene top phase during the first two washings with fresh toluene. However, there was no further migration of interfacially active material into the toluene phase after the second washing of the bitumen film. For the case of toluene collected from the top phase of an asphaltene film, the interfacial pressure remains close to zero upon compression of the newly formed toluene/water interface as shown in curve (d) of Figure7.11. The results of Figure 7.11 indicate that the

collected toluene top phases from maltene and bitumen films contain surface-active material, which can adsorb from the collected toluene at the toluene/water interface upon contacting with fresh water. The collected toluene from the top phase of an asphaltene film does not contain any interfacially active material and thus resulted in unnoticeable interfacial pressures upon compression. These results indicate that interfacially active material migrated from the prepared bitumen and maltene films to the toluene top phase. However, for the asphaltene case no interfacial active material migrated from toluene/water interface to the bulk toluene top phase.

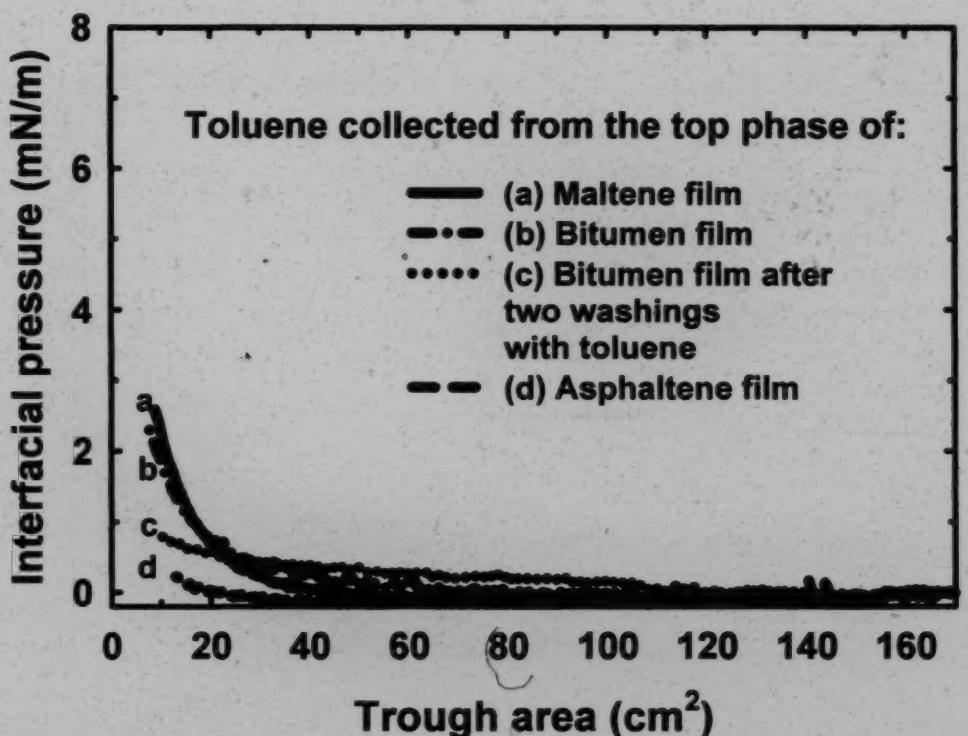

Figure 7.11. Interfacial pressure-area isotherms using toluene collected from the top phase of: (a) a maltene film; (b) a bitumen film; (c) a bitumen film after two washings with fresh toluene; (d) an asphaltene film.

Figure 7.12 shows interfacial pressure-area (π-A) isotherm of a bitumen film formed by spreading 1000 μL of bitumen-in-toluene solution (1mg/mL) at the toluene/ water interface, curve (a), and (π-A) isotherm recorded upon compression of the interface created by top phase toluene collected from (a) on fresh water surface, curve (b). In these experiments a 1000 μL of bitumen-in-toluene solution at concentration 1mg/mL was spread onto water surface. After 10 minutes, the formed film was covered by toluene top phase. Then, after 30 minutes, the film was compressed and the isotherm (a) was recorded. After the compression, the toluene top phase was collected and placed onto the fresh water surface. After 30 minutes, the interface was compressed and isotherm (b) was recorded. Isotherm (a) is seen to rise steeply upon compression, indicating close packing of the bitumen molecules at the interface. The collected top phase toluene contained the excess of bitumen material dissolved in toluene, which adsorbed at the interface once it was placed onto the fresh water.

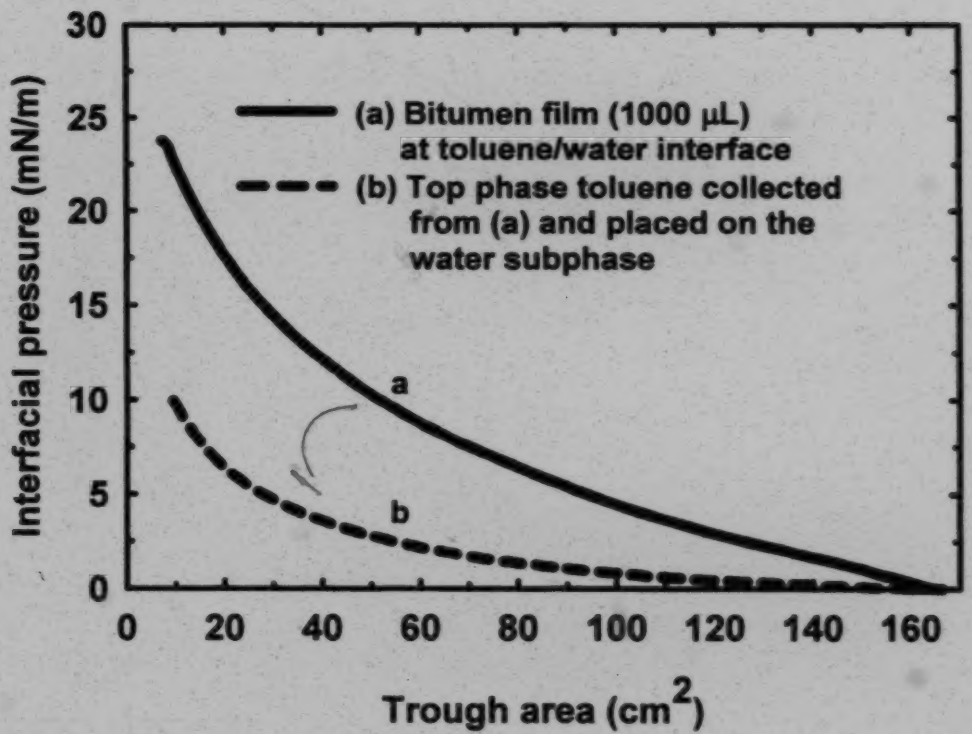

Figure 7.12. Interfacial pressure-area (π-A) isotherms of (a) a bitumen film formed by spreading 1000 µL of bitumen-in-toluene solution (1mg/mL) at toluene/water interface and (b) top phase toluene collected from (a) and placed on the fresh water surface.

To evaluate the possibility of migration of bitumen interfacial material from the interface to the water subphase, the subphase was checked for interfacial activity. The tests were conducted as follows: a bitumen film was prepared as described earlier at the toluene/water interface and compressed to an interfacial pressure of ~20 mN/m. The two barriers were then fully expanded. Next, the toluene top phase and the bitumen film were removed; the subphase water was collected and placed into a clean trough. A fresh toluene top phase was then placed on the collected water surface. The formed toluene/water interface was compressed after 30 minutes of equilibration. In Figure 7.13,

the pressure–area (π-A) isotherm obtained upon compression showed interfacial pressures close to zero. This finding indicates that there was only negligible amount of surface active material migration from the prepared bitumen film to the water subphase.

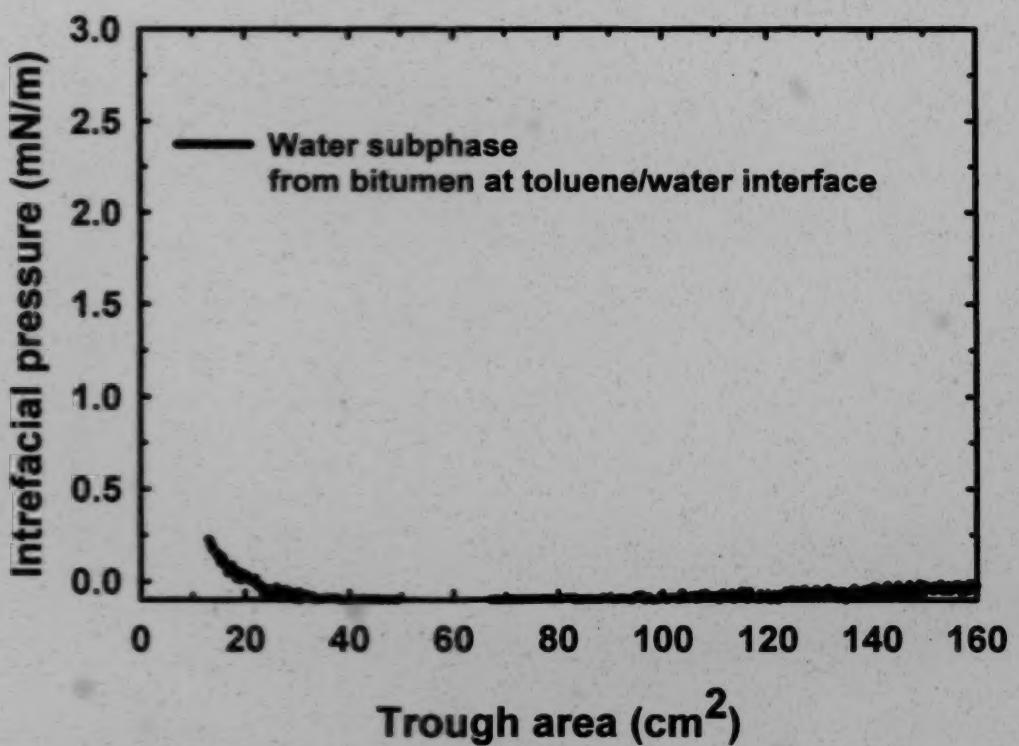

Figure 7.13. Interfacial pressure-area (π-A) isotherm recorded on compression of fresh toluene/water after being used as a liquid subphase for bitumen film interface.

7.2.1 Nature of Bitumen Interfacial Films at Toluene/Ultrapure Water Interface.

Figure 7.14 shows a comparison of the (π-A) isotherms for a bitumen monolayer subjected to two washings with fresh toluene with that of an asphaltene monolayer. The interfacial pressure–area (π-A) isotherm of the bitumen film after two washings is nearly identical to that of the original asphaltene monolayer. When we take

into account that the actual bitumen used in this study contained about 15% asphaltenes and the fact that the asphaltene film prepared is about 15% of the mass of the prepared bitumen film, it can be concluded that the bitumen film at toluene/water interfaces is composed mainly of asphaltenes.

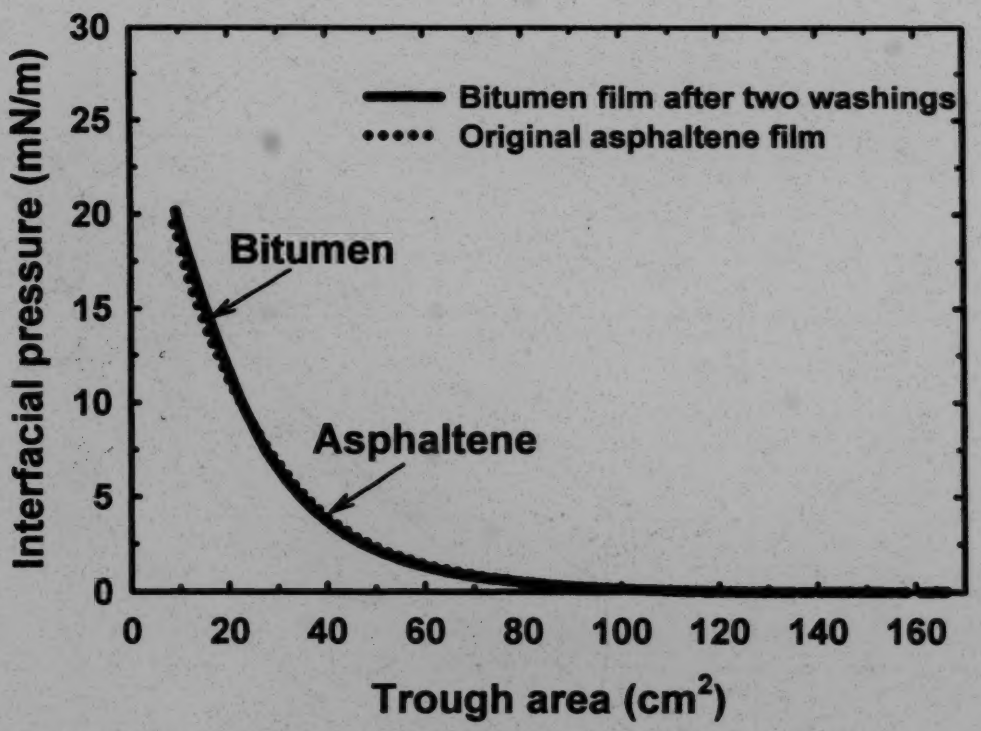

Figure 7.14. Comparison of interfacial pressure-area (π-A) isotherms of a bitumen monolayer after two washings with fresh toluene with that of an original asphaltene monolayer at the toluene/water interface.

7.3. Washing of Bitumen, Asphaltene, and Maltene Films at Toluene/Recycle Process Water Interfaces

To make the experimental conditions more relevant to the industrial case, the monolayer properties of interfacially active substances of bitumen, asphaltene and maltene were measured at toluene/Aurora plant recycle process water interface. These measurements are important for verification of possibility of the interactions between molecules in the monolayer and various species dissolved in the recycle process water. Composition and properties of the process water are given in Table 7.1.

Table 7.1: Comparison and properties of the Aurora plant recycle process water. Adapted from Zao et al. (2006).

Aurora Plant Recycle Process Water **Composition and Properties** (2003)			
Ion	**Concentration mg/L**	**Concentration meq/L**	**Total**
Na^+	550.00	23.9	
K^+	15.50	0.40	
Mg^{++}	20.00	1.65	
Ca^{++}	49.10	2.46	
			28.4
Cl^-	450.00	12.7	
SO_4^{2-}	202.00	4.21	
CO_3^{2-}	66.00	2.20	
HCO_3^-	630.00	10.3	
			29.4
pH		7.8~8.5	
Conductivity (mS/cm)		2.1±0.2	
Surface Tension (γ) (mN/m)		63.4~68.9	

Before each new test, the lower compartment of the trough was filled with the

ultrapure water. After compressing the clean water surface, to insure that the trough is clean, the initial subphase was carefully removed and replaced with the process water. The rest of the experiment was conducted following the standard procedure.

It is shown in Figure 7.15 that interfacial pressure/area isotherms of bitumen, asphaltene and maltene at toluene/process water interface follow the same trend as those at toluene/ultrapure water interface (Figure 7.1). The interfacial pressure-area (π-A) isotherm of the maltene film lies below that of the asphaltene and bitumen films. The highest attainable interfacial pressure for maltene film is lower than that for the asphaltene and bitumen films, indicating higher compressibility and less surface active material of the maltene film at the toluene/process water interface.

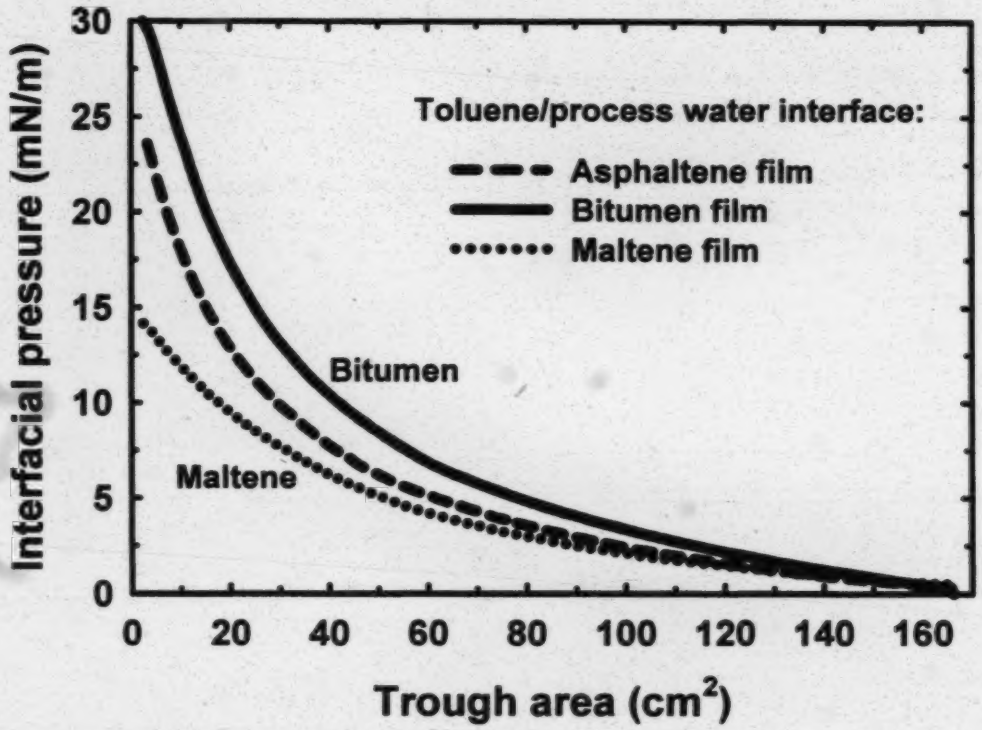

Figure 7.15. Comparison of interfacial pressure-area (π-A) isotherms of bitumen, asphaltene, and maltene monolayers at toluene/recycle process water interface.

To study adsorption reversibility of surface-active components, Langmuir films of bitumen, maltene, and asphaltene were prepared at a toluene/recycle process water interface. These films were subjected to multiple washings with toluene. Asphaltenes were found to be irreversibly adsorbed at the toluene/process water interface because only a slight change in interfacial pressure-area isotherms was observed when asphaltene films were repeatedly washed with toluene, as shown in Figure 7.16. In the case of bitumen films, the pressure-area isotherms showed a consistent shift upon the first two consecutive washings, as seen in Figure 7.17. No further shift was observed when the bitumen film was further washed. Isotherms recorded after two washings were very similar to that of an original asphaltene film at toluene/process water interface as shown in Figure 7.18. This type of π-A isotherms would indicate that the bitumen film present at the toluene/process water interface was mainly composed of asphaltenes with some entrained surface active materials from maltene (as it was observed for the toluene/ultrapure water interface). For a maltene film at toluene/recycle process water interface, consecutive washings with fresh toluene showed a progressive loss of maltenes from the interface, as shown in Figure 7.19.

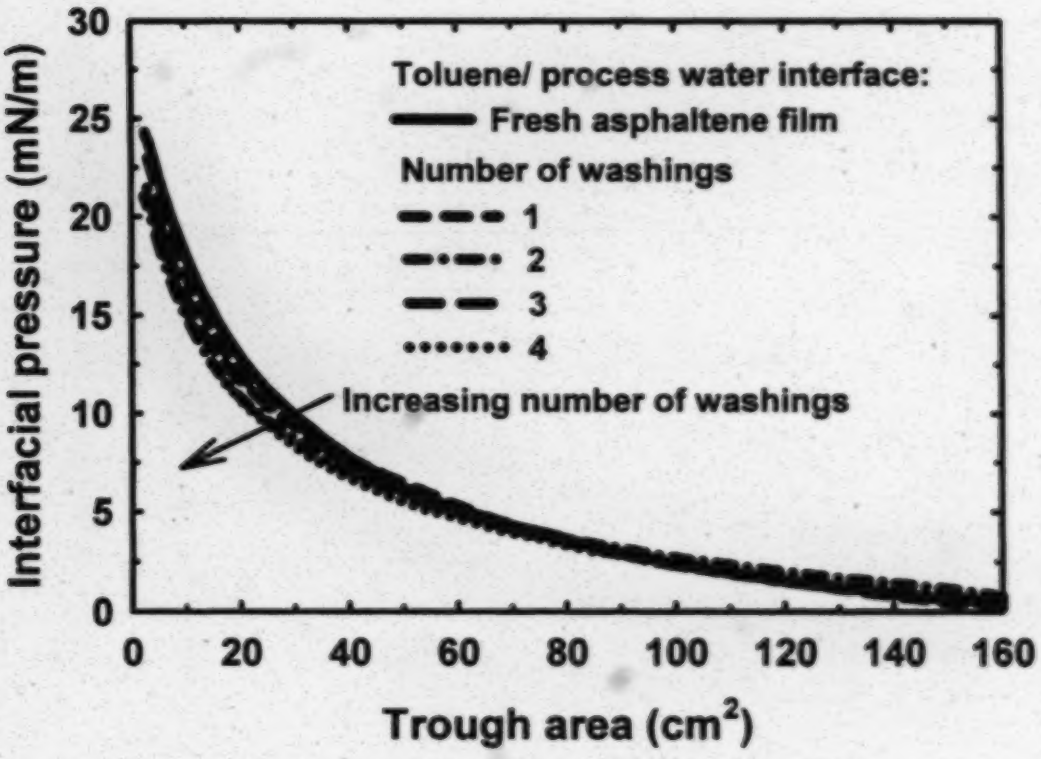

Figure 7.16. Effect of washing an asphaltene film with fresh toluene on interfacial pressure-area isotherms for the toluene/process water interface.

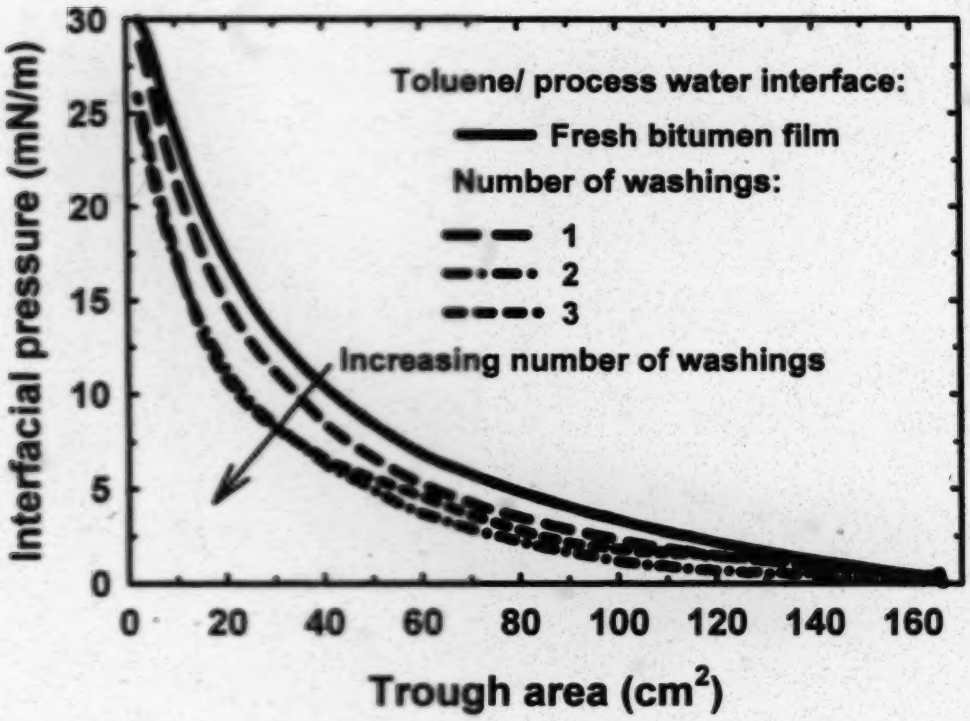

Figure 7.17. Effect of washing a bitumen film with fresh toluene on interfacial pressure-area (π-A) isotherms for toluene/process water interface.

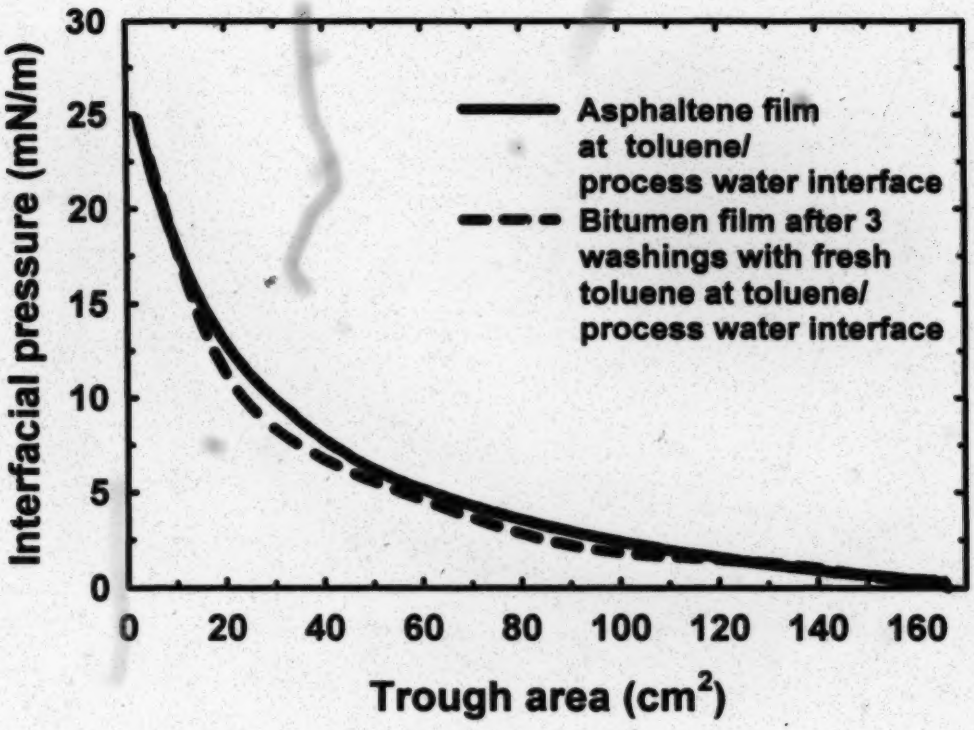

Figure 7.18. Comparison of interfacial pressure-area (π -A) isotherm of an original asphaltene monolayer at the toluene/process water interface with that of bitumen monolayer after three washings with fresh toluene.

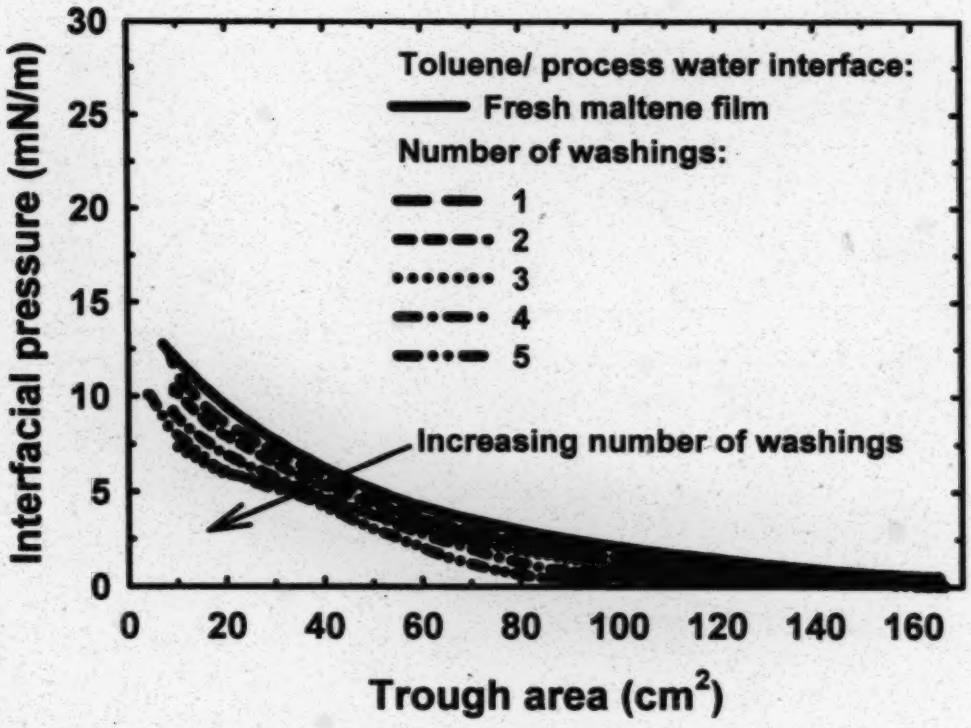

Figure 7.19. Effect of washing a maltene monolayer with fresh toluene on interfacial pressure-area (π-A) isotherms for toluene/process water interface.

As it was discussed above, the same changes in the interfacial pressure-area π-A isotherms upon washing of bitumen, asphaltene and maltene films with toluene were observed when process water instead of ultrapure water was used as the subphase. However, there was a slight deviation for the isotherms recorded using toluene collected from the top phase from a maltene film, a bitumen film, and an asphaltene film at toluene/process water interface and placed onto ultrapure water (Figure 7.20). Unlike the case of toluene collected from the top phase from the asphaltene at the toluene/ultrapure water interface, the toluene top phase recovered after asphaltene film compression at the toluene/process water interface indicated the presence of some interfacially active

material. However, the interfacial pressure-area profile for the toluene/process water interface without monolayer (curve (d)), was nearly identical to the isotherm (a). The fact that the collected top phase for the asphaltene film and that of toluene/process water gave same π-A isotherms would indicate that no additional surface active materials from asphaltenes initially present migrated to the toluene phase. Isotherms (b) and (c) indicated that the collected toluene top phases from bitumen and maltene films contain interfacially active materials which adsorbed from the collected toluene at the toluene/water interface upon contacting with ultrapure water.

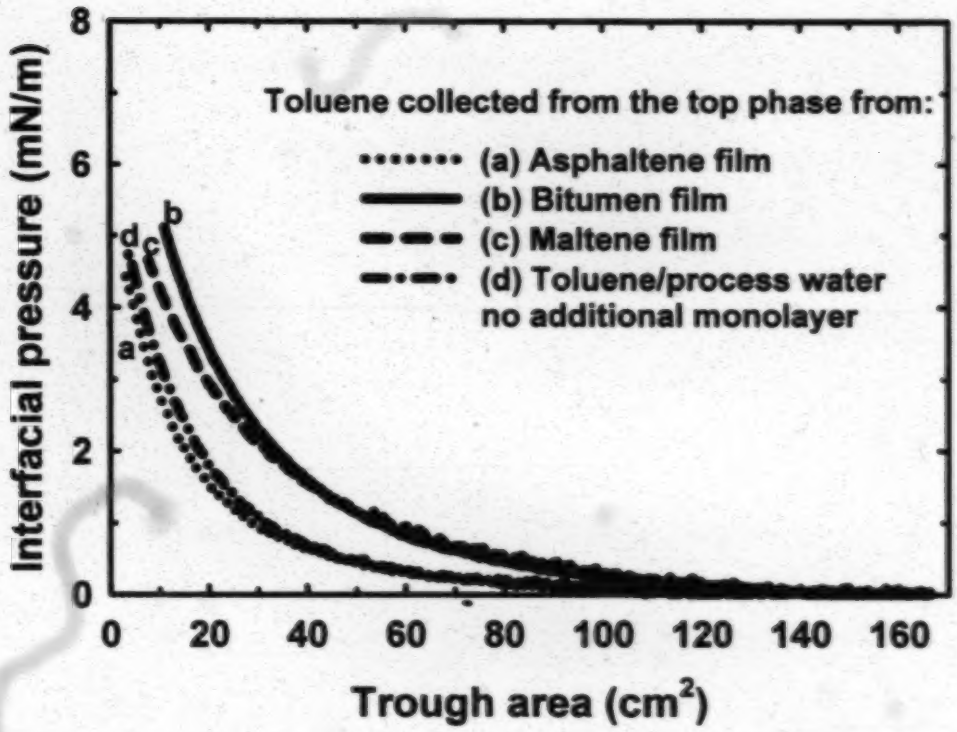

Figure 7.20. Interfacial pressure-area (π-A) isotherms recorded using toluene collected from the top phase from (a) an asphaltene film, (b) a bitumen film, (c) a maltene film at

toluene/process water interface and (d) toluene/process water interface with no additional monolayer present.

7.4. Experimental Study of the Adsorption Reversibility. Summary

Before moving on to studies involving any chemical additives which can serve as potential demulsifiers, an attempt was made to remove the material adsorbed at the interface by diluting it with fresh toluene. Bitumen, asphaltene and maltene films subjected to multiple washings with fresh toluene exhibited different behavior. Multiple washings of an asphaltene film did not show any distinguishable difference in the recorded isotherm after each washing. Even though bitumen is known to be completely soluble in toluene, it was impossible to remove the adsorbed asphaltene material by diluting it with fresh toluene. Further studies have to involve chemical additives which would be able to interact with the asphaltene surface active material.

7.5. References

(1) Zhang, L. Y., Lopetinsky, R., Xu, Z., Masliyah, J. H. Asphaltene Monolayers at a Toluene/Water Interface. *Energy & Fuels*. **2005**, *19*, 1330-1336.

Chapter 8

Effect of Salts, pH and Miscible Solvent in Aqueous Phase

In addition to the solvent phase, interfacial film properties also depend on the composition of the aqueous phase. The influence of aqueous phase pH and chemical additives on the compressibility of bitumen films is considered in this chapter. Comparison is made with the results obtained using recycle process water as the subphase.

As shown in the previous chapter, the results obtained for bitumen, asphaltene and maltene films at toluene/recycle process water (pH 8.2) interface showed that the films became more closely packed than at toluene/ultrapure water at either pH 5.8, or 8.2. The Aurora plant recycle process water itself was found to contain a considerable amount of interfacially active components.

It was demonstrated that, at an elevated pH of the water subphase and in the presence of calcium ions, the rigidity of bitumen film increases. The AFM images of the obtained LB films showed a coarse deposition.

The highest interfacial pressures created by bitumen interfacial films were observed at the highest pH of the water subphase (pH = 11). Lowering the pH of the water subphase to 3 or 4 also caused an increase in the interfacial pressure values but to a little extent.

Using a mixture of acetone and water and sodium naphthenate as an additive to water helped decrease the bitumen interfacial activity, causing a remarkable decrease in interfacial pressures for the case of a bitumen monolayer.

8.1. Using Aurora Plant Recycle Process Water as the Aqueous Subphase

Using the industrial process water as an aqueous subphase can help to create conditions more similar to the industrial process, and to examine the sensitivity of bitumen film to changes in the composition of the liquid subphase. This section provides a comparative study for bitumen, asphaltene and maltene films prepared at toluene/ultrapure water (pH 5.8) interface and those prepared at toluene/recycle process water interface (pH 8.2).

Figure 8.1 shows results obtained for bitumen film at toluene/ultrapure water interface at pH 5.8 (a), toluene/recycle process water interface at pH 8.2 (b), and toluene/ultrapure water interface at pH of 8.2 (c). The shape of curve (a) is slightly different from curves (b) and (c). However, increasing pH of the ultrapure water to the level of that of the process water did not have the same effect on the bitumen film. It can be seen from Figure 8.1 that interfacial pressure increased to a greater extent when process water was used as the subphase. The maximum attainable interfacial pressure was raised up to ~ 30 mN/m for process water compared to 20 mN/m for the case of ultrapure water subphase at pH 5.8, and 25 mN/m in the case of ultrapure water at pH 8.2. Judging from the experimental results shown on Figure 8.1, the difference between the films at ultrapure water and process water can not be fully explained by the pH effect. The observed difference can be attributed to the presence of inorganic ions and, most likely, other surface active components in the process water.

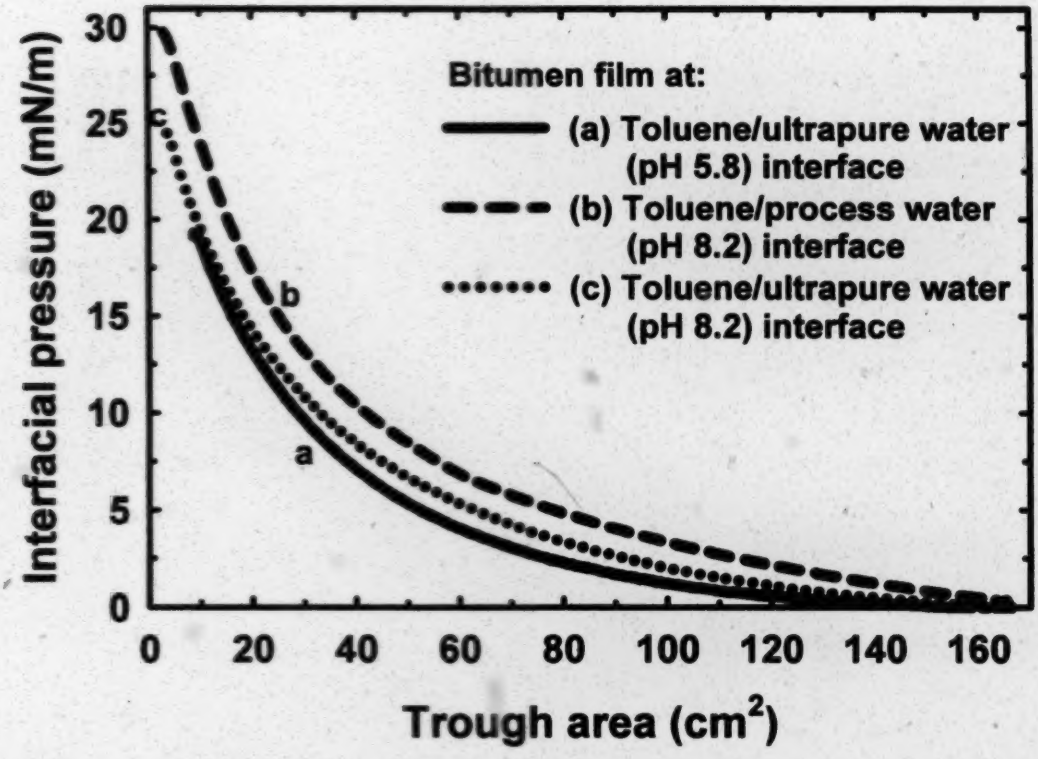

Figure 8.1. Comparison of the interfacial pressure-area (π-A) isotherms of bitumen films at toluene/ultrapure water (pH 5.8) interface, toluene/recycle process water (pH 8.2) interface, and at toluene/ultrapure water at elevated pH to 8.2.

Three similar tests were performed for asphaltene films. Figure 8.2 shows a comparison of the pressure-area isotherms for asphaltene film at the interfaces of (a) toluene/ultrapure water at pH 5.8, (b) toluene/process water at pH 8.2, and (c) toluene/ultrapure water at pH 8.2. In Figure 8.2, isotherms for the interface of toluene/ultrapure water at pH 5.8 (a) and pH 8.2 (c) are almost identical. Increasing pH of the water to 8.2 did not impact the behaviour of asphaltene films. The level of subphase pH investigated was not sufficient to affect the asphaltene film. However, in

the case of the process water subphase, curve (b) shifted toward the higher interfacial pressure values upon area reduction. In this case, the interfacial pressure began to rise upon the compression and reached the higher value, showing the presence of larger amount of interfacially active material than in the case of bitumen film on ultrapure water.

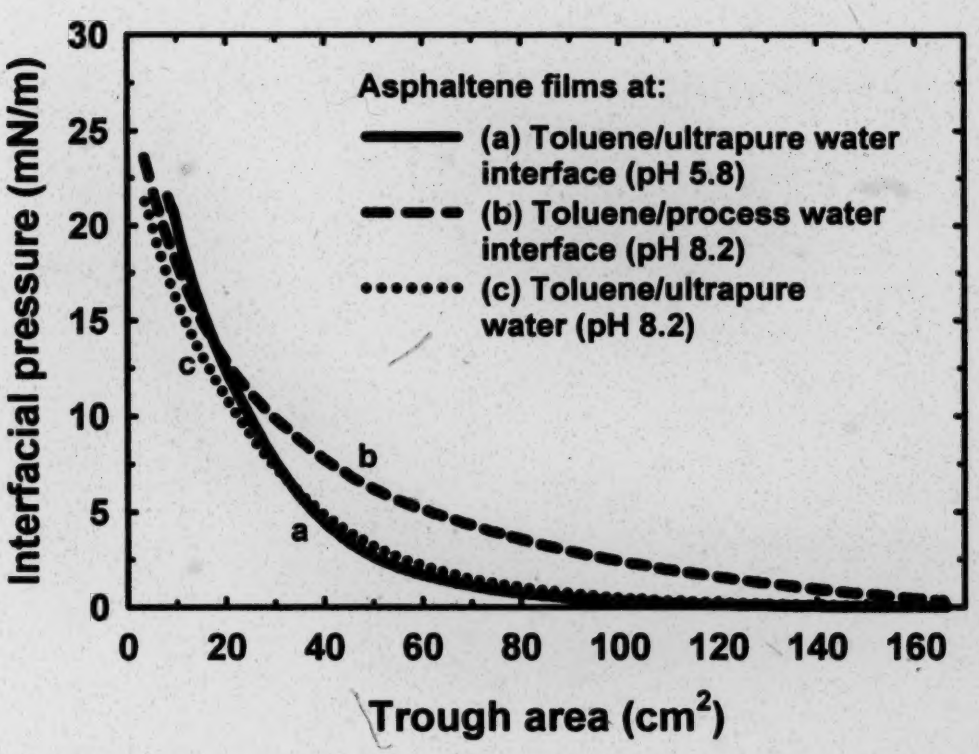

Figure 8.2. Comparison of the interfacial pressure-area (π-A) isotherms of asphaltene films at (a) toluene/ultrapure water (pH 5.8) interface, (b) toluene/recycle process water (pH 8.2) interface, and at (c) toluene/ultrapure water at elevated pH to 8.2.

Judging from the results described above, it was most likely that the process water itself contained some interfacial active components. When the ultrapure water

subphase was replaced by the Aurora plant recycle process water, the interfacial pressure-area isotherms recorded for bitumen and aspheltene films shifted towards larger areas and higher pressures, implying that there were more materials at the interface.

The experiments were conducted to check whether the process water has any interfacial activity. At the beginning of each test, the position of the barriers was zeroed at their maximum extension. When compressing a clean toluene/ultrapure water interface, the interfacial pressure readings remained at zero with area reduction as shown in Figure 8.3. The recorded isotherm upon compression of toluene/process water interface (Figure 8.3) shows an immediate rise in interfacial pressure. This increase in the interfacial pressure was caused by typical decrease of the surface tension of water, indicating the presence of surfactants in the process water.

Figure 8.4 shows the AFM images of LB films deposited from toluene/ultrapure water (pH 5.8) interface and toluene/process water interface without addition of surface active materials. Image (a) in Figure 8.4 shows a smooth surface without deposition of any materials from the toluene/ultrapure water interface. Image (b) indicated presence of randomly distributed molecular aggregates deposited from the process water. These topographic images confirmed presence of a considerable amount of the interfacial material adsorbed from the process water.

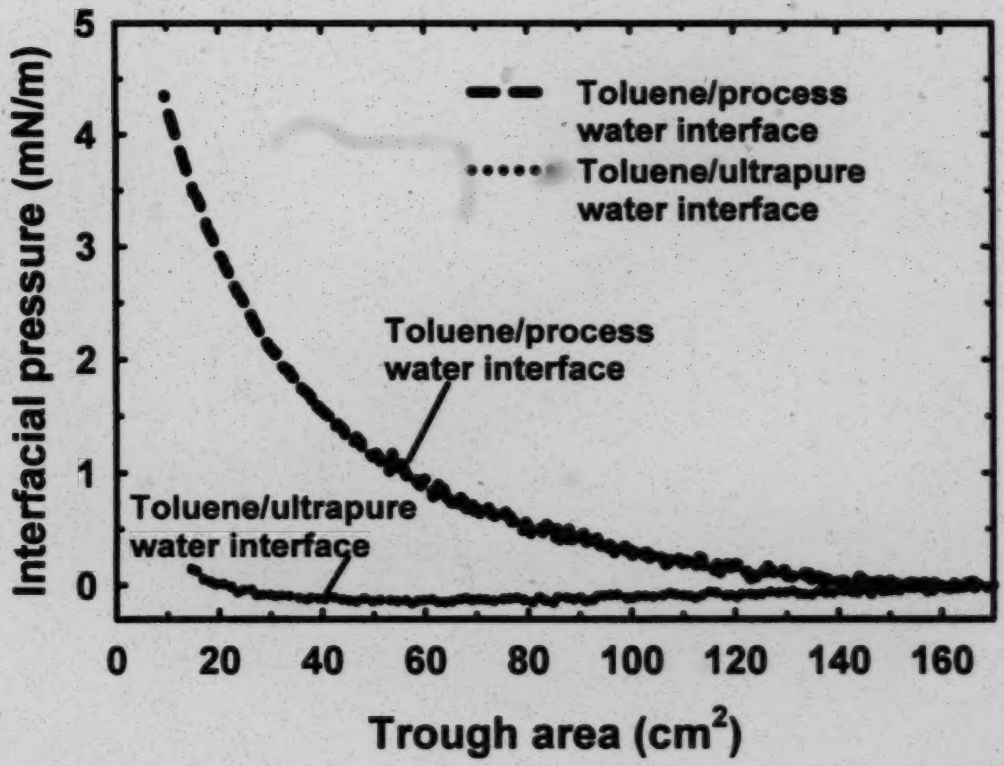

Figure 8.3. Comparison of interfacial pressure-area (π -A) isotherms recorded upon compression of toluene/recycle process water and toluene/ultrapure water interfaces.

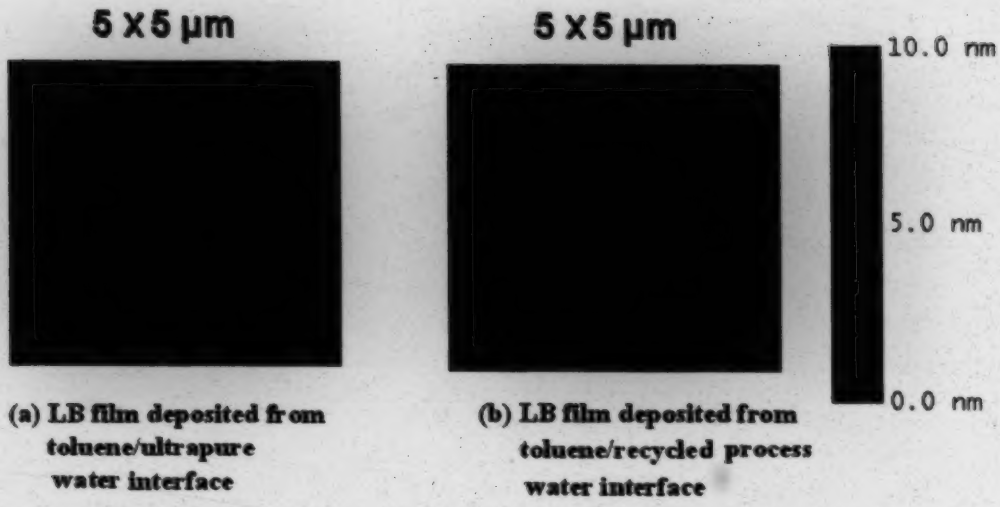
5 x 5 µm
5 x 5 µm
10.0 nm
5.0 nm
0.0 nm
(a) LB film deposited from toluene/ultrapure water interface
(b) LB film deposited from toluene/recycled process water interface

Figure 8.4. Comparison of AFM images obtained for the LB films deposited from (a) toluene/ultrapure water interface and (b) toluene/recycle process water interface.

8.2. Effect of Water Phase pH

Experiments were conducted to study the effect of water phase pH on the compressibility of bitumen interfacial films. The pH level of the water subphase was adjusted by adding NaOH or HCl solutions to ultrapure water. The corresponding changes in the interfacial pressure-area (π-A) isotherms as a function of sub aqueous pH are shown in Figure 8.5. At the beginning of the compressions there is little difference in the recorded isotherms. At pH 3, 4, 8.5, all the π-A isotherms were almost identical. However, at pH 11, the π-A isotherm exhibited a higher pressure at a given area. In the case of pH 11, the rise in the interfacial pressure begins at an earlier stage of compression. For the bitumen film at toluene/water interface, high subphase pH drastically affects the shape of the interfacial pressure-area (π-A) isotherm.

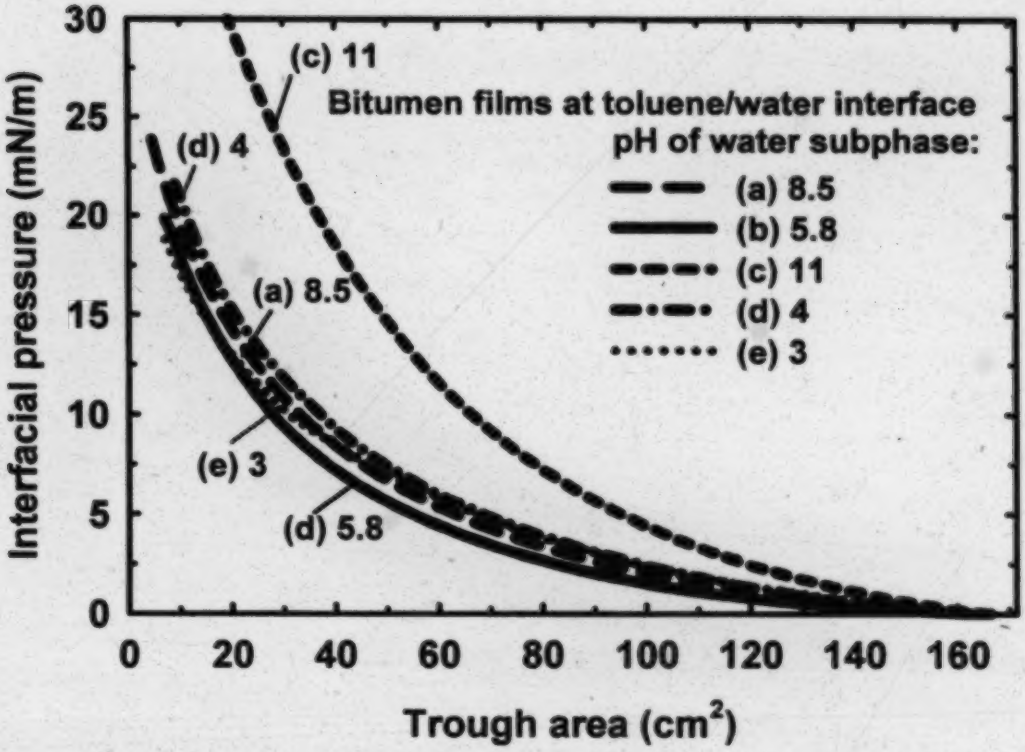

Figure 8.5. Interfacial pressure-area (π-A) isotherms of bitumen films at toluene/water interface at different pH of the water phase: (a) 8.5, (b) 5.8, (c) 11, (d) 4, (e) 3.

8.3. Effect of Calcium at High Water Phase pH

An attempt was made to saturate the subphase with calcium by using high dosage at 600 ppm, and then to deposit a bitumen monolayer on the water surface. The interfacial pressure-area isotherm of bitumen at the interface of toluene/water saturated with calcium at pH of 8.2, (a) on Figure 8.6, was compared to isotherms of bitumen films at toluene/ultrapure water interface at pH 5.8 (b) and 8.2 (c). An increase in the interfacial pressures was observed for the isotherm measured when the subphase was saturated with calcium, as compared to the isotherms without calcium addition.

Similar effect of calcium ions in water phase can be seen in Figure 8.7 for a bitumen film formed after spreading a larger amount (600 μL) of 1mg/mL bitumen-in-toluene solution. The presence of divalent cations (such as Ca^{2+}) makes the films more closely packed and more hydrophobic (Gaines, 1966).

Bitumen film, prepared using 600 μL bitumen-in-toluene solution, was imaged using atomic force microscopy. The AFM image in Figure 8.8 shows the deposition of large aggregates; possibly due to the conversion of RCOOH in bitumen to calcium-based salt precipitates. Saturation of the water subphase with calcium led to the incorporation of calcium ions within the film. High local concentration of calcium ions initiated the precipitation. The film deposited onto a silicon wafer was visible by naked eye. AFM image for this film revealed the presence of large aggregates with a height of ~ 300 nm.

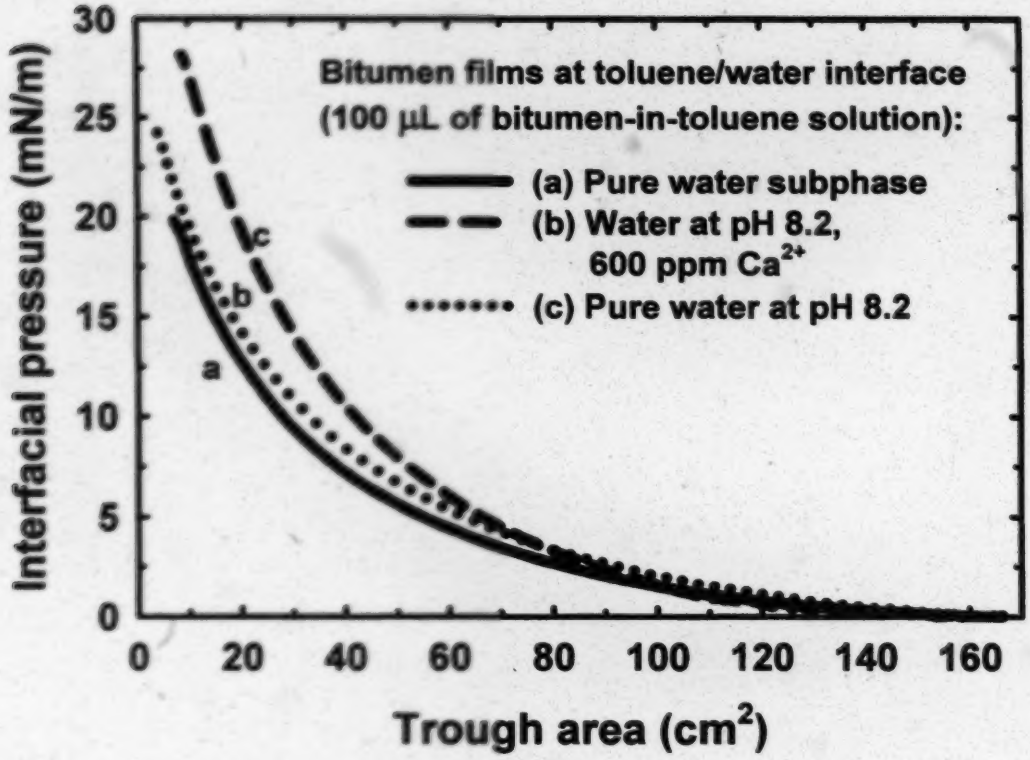

Figure 8.6. Comparison of interfacial pressure-area (π-A) isotherms of bitumen films, created by spreading 100 µL bitumen-in-toluene solution, at (a) toluene/ultrapure water interface pH 5.8, (b) toluene/water at pH 8.2 with 600 ppm calcium, and (c) toluene/ water pH 8.2.

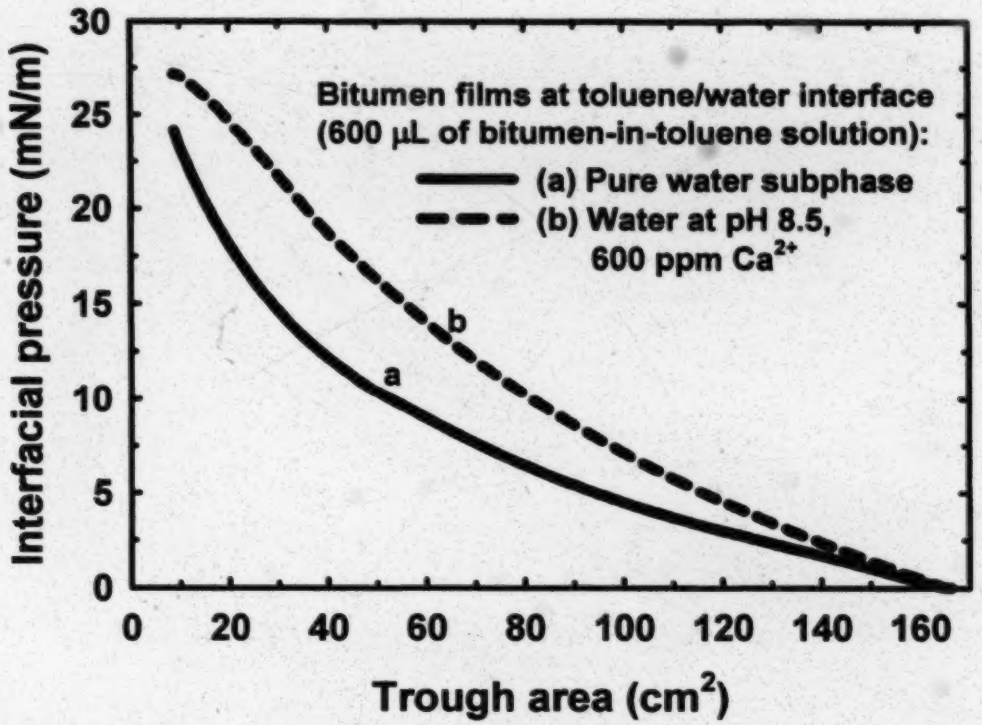

Figure 8.7. Comparison of interfacial pressure-area (π-A) isotherms of bitumen films, created by spreading 600 µL bitumen-in-toluene solution, at the (a) toluene/ultrapure water interface pH 5.8, (b) toluene/water at pH 8.2, 600 ppm calcium interface.

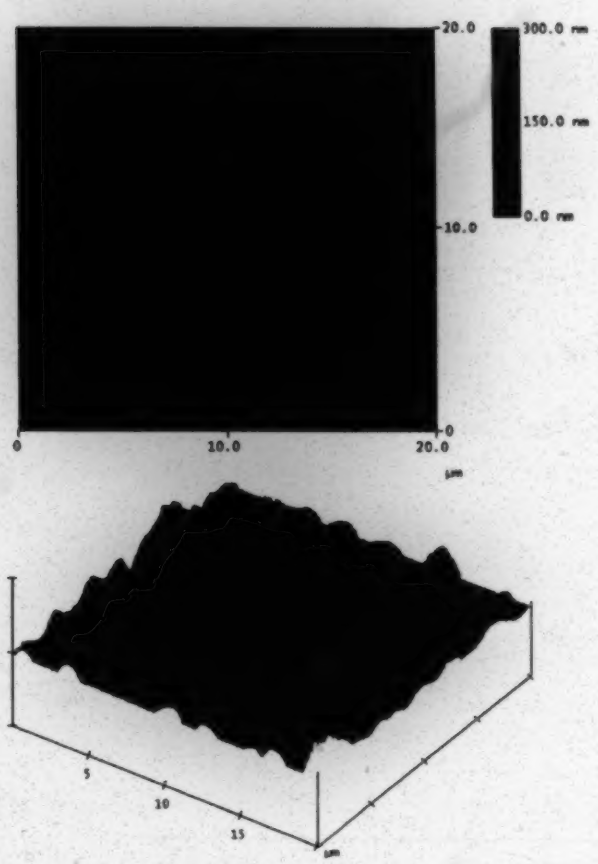

Figure 8.8. AFM topographic image of bitumen film created by spreading 600 μL bitumen-in-toluene solution onto water at pH 8.2, 600 ppm calcium.

8.4. Effect of Acetone Addition to Water Phase

A detectable amount of heavy metals, such as Vanadium and Nickel, are found in asphaltenes and resins in various forms of organic species. Presumably they are present in the form of complexes with various porphyrins, which can be eluted with acetone (Saitoh, 2001). Porphyrin and metalo-porphyrin complexes are naturally occurring emulsifiers. Their molecules have a flat plate-like structure that pack at oil/water interface, producing dense interfacial films (Canevari, 1982). In this work, certain

amount of acetone was mixed with the water subphase to study its effect on the bitumen film properties. Figure 8.9 shows the isotherms of bitumen films at air/water-acetone interfaces. In this set of measurements, acetone was first mixed with ultrapure water and placed into the Langmuir trough. Then, 100 μL of bitumen-in-toluene solution of 1 mg/mL was spread onto the surface of the acetone and water mixture. After 10 minutes, the film was compressed at air/acetone-water interface. Unlike in previous experiments, where acetone was added to the toluene top phase, in the case of acetone addition to the water phase, some of the monolayer-forming materials such as metal-porphyrins, which are not soluble in acetone (Saitoh, 2001), were carried into the aqueous phase to become precipitates rather than appearing at the interface. This condition was reached when acetone volume was 25% of the aqueous phase.

At 10% of acetone in water, the interfacial pressure created by the bitumen film at the air/acetone-water interface rises quite steeply over a small trough area values, showing a very rigid surface. On the water surface, small black spots were visible to the naked eye. A possible explanation for this observation would be that the porphyrin complexes were eluted with acetone, but remained at the interface instead of being carried into the subphase.

Figure 8.10 shows isotherms recorded for bitumen films at air/acetone-water (1:1 volume ratio) interface. In this experiment, the possibility of removing the already formed bitumen film from the air/water interface was studied. For isotherm (a), acetone was mixed with water and placed into the Langmuir trough. Then, 100 μL of bitumen-in-toluene solution (1mg/mL) was spread onto the surface. After 10 minutes, the film was compressed. For isotherm (b), the trough was filled with water. Then, 100 μL of

bitumen-in-toluene solution was spread onto water surface. After 10 minutes, 50% of the water volume was removed from underneath of the formed bitumen monolayer and replaced with pure acetone. The acetone that was added to the aqueous phase was able to remove the bitumen film from the interface. Both isotherms (a) and (b) exhibit zero-surface pressure upon compression. As a sufficient amount of acetone is added, the measured surface pressure upon compression of a bitumen film will eventually become zero.

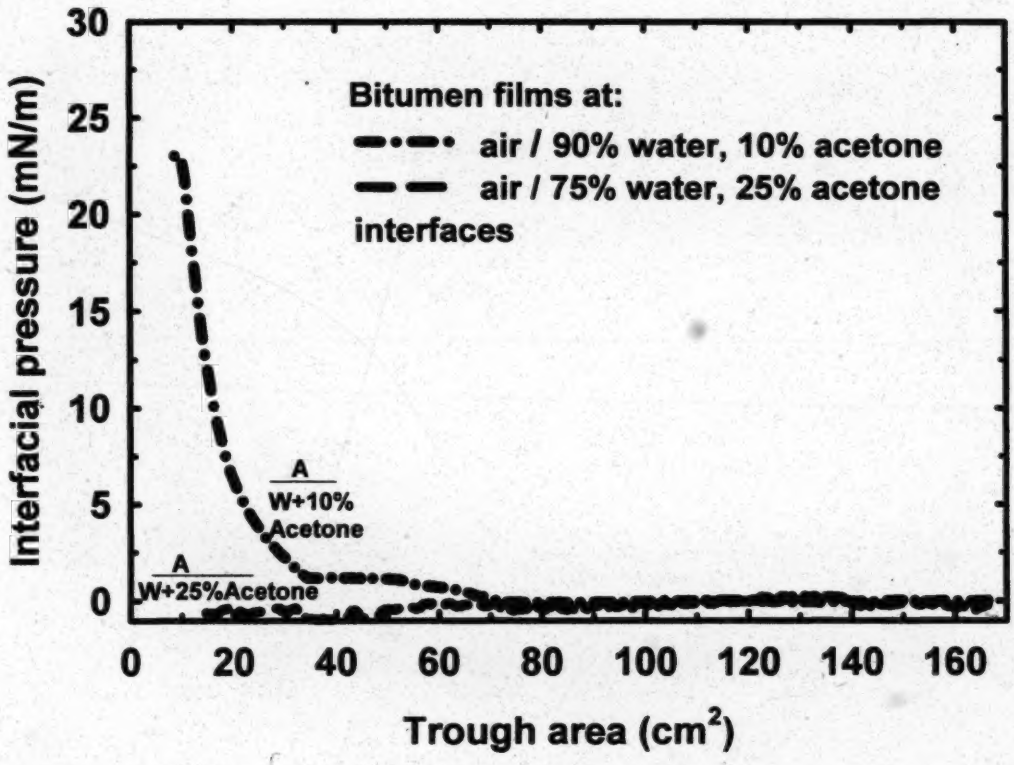

Figure 8.9. Interfacial pressure-area isotherms of bitumen films (100 μL of bitumen-in-toluene solution) at the interface of air/water-acetone mixture at 9:1 and 3:1 volume ratios.

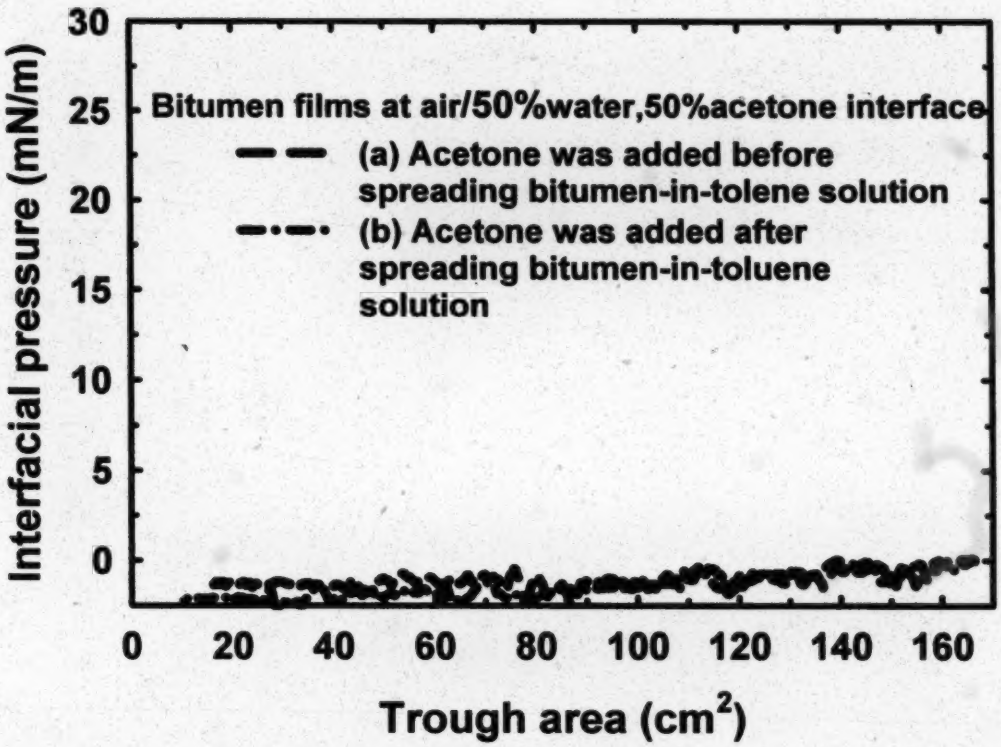

Figure 8.10. Interfacial pressure-area (π-A) isotherms of bitumen films (100μL of bitumen-in-toluene solution 1mg/mL) at air / 50%water, 50% acetone interfaces. (a) Acetone was added (acetone was mixed with water) before spreading bitumen-in-toluene solution, (b) Acetone was added during the subphase exchange underneath the formed film.

8.5. Effect of Sodium Naphthenate Addition to Water Phase

Some chemical additives of interest in bitumen film destabilization are interfacially active. Sodium naphthenate, for example can adsorb at the toluene/water interface and in this way reduce the bitumen film rigidity by partial replacement of the film (Wu, 2003). Figure 8.11 compares isotherms of bitumen film at toluene/water interface with (a) and without (b) sodium naphthenate (1g/L) addition. Isotherm (a)

enters "liquid extended" state at area value of ~40 cm^2 , whereas isotherm (b) enters this state at 130cm^2. The presence of sodium naphthenate in water phase at the concentration of 1g/L can affect the state of bitumen film to this large extent. Addition of sodium naphthenate increases bitumen film compressibility and reduces the maximum attainable interfacial pressure values.

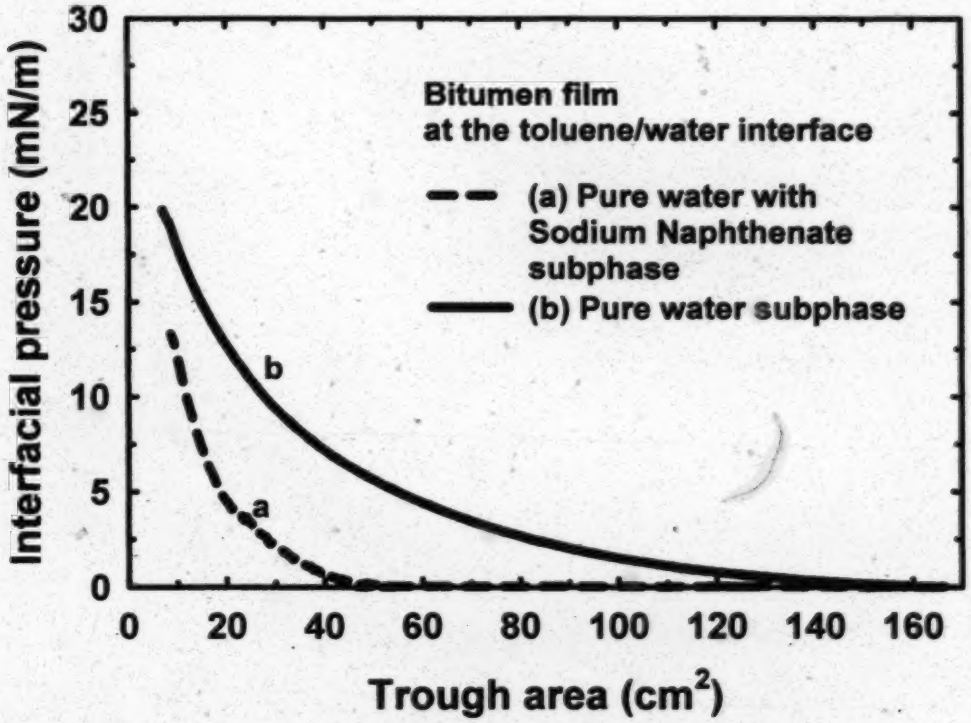

Figure 8.11. Interfacial pressure-area (π-A) isotherms of bitumen films at (a) toluene/ultrapure water with sodium naphthenate interface and (b) toluene/water interface.

8.6. Effect of Salts, pH and Miscible Solvent in Aqueous Phase. Summary

The experiments involving recycle and ultrapure water usage as a subphase showed impact of the water quality (pH and salinity) on bitumen film compressibility.

Calcium ions presence and high water pH were found to have negative impact on bitumen film properties.

The results of experiments conducted for bitumen interfacial films with and without chemical additives in the subphase showed promising tendency of some chemicals (acetone, sodium naphthenate) to decrease bitumen interfacial activity. In future studies, a step towards understanding the interaction between chemical additives and a Langmuir monolayer can be taken.

8.7. References

(1) Gaines, G. L. Jr. On the History of Langmuir-Blodgett films. *Thin Solid Films.* **1983**.

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Chapter 9

Summary

The thesis is concerned with the interfacial behaviour of bitumen, asphaltene and maltene films at solvent/water interfaces.

Langmuir and Langmuir-Blodgett (LB) films of Athabasca bitumen were studied using the Langmuir interfacial trough and the Atomic Force Microscope (AFM). We obtained isotherms representing the dependency of the interfacial pressure on the film area and the AFM images of the LB films deposited onto solid substrates. Both the isotherms and the AFM images were used to understand molecular behaviour at interfaces.

To study the adsorption reversibility of bitumen components, Langmuir films of bitumen, maltene, and asphaltene prepared at a toluene/ultrapure water interface were subjected to multiple washings with toluene. Asphaltenes were found to be irreversibly adsorbed at the toluene/water interface. For repeated washing of bitumen films, irreversible adsorption was indicated after two consecutive washings. Both the isotherms recorded after two washings and the AFM images of the interfacial material, showed that the bitumen film present at the toluene/water interface was mainly composed of asphaltenes. For maltene films, consecutive washings showed a progressive loss of maltenes from the toluene/water interface into the washing toluene. Similar results were obtained for the asphaletene, bitumen and maltene films subjected to washing with toluene at the toluene/recycle process water interface.

The results of this research showed the influence of the nature of bulk oil and water phases on bitumen film interfacial properties.

When replacing the ultrapure water subphase with the Aurora plant recycle process water, bitumen, aspheltene and maltene films became more closely packed. Studying Langmuir and LB films for toluene/recycle process water (with no additional interfacial film) confirmed the presence of the considerable amount of interfacially active materials in the recycle process water.

Studying the influence of the top phase solvent composition on bitumen film compressibility, it was found that the film rigidity increased with increasing heptane content in a heptane-toluene mixture. When a mixture of toluene and acetone was used as the oil phase, the interfacial bitumen film became more compressible.

It was demonstrated that, at an elevated pH of the water phase, the presence of calcium ions increased the rigidity of bitumen films. The AFM images of the LB films showed the deposition of large molecular aggregates, most likely in the form of calcium salt precipitates.

The highest interfacial pressures created by the bitumen interfacial films were observed at the highest pH of the water phase tested. On the contrary, the addition of acetone or sodium naphthenate to the water phase decreased bitumen interfacial activity, causing a remarkable decrease in the interfacial pressures created by bitumen monolayers.

The described experiments showed that changes in the composition of subphase and top phases led to changes within the film itself due to complex interactions between the molecules at the interface and those in the bulk phases.

9.1. Recommended Future Studies

Interfacially active components accumulated at an oil/water interface promote the formation of interfacial films which resist droplets coalescence. Under these conditions oil/water phase separation becomes extremely difficult. Therefore studying interfacial films is crucial in understanding the stabilization mechanisms of water-in-bitumen emulsions. In the present work, interfacial behaviour of bitumen, maltene, and asphaltene films was studied at oil/water interface. Multiple washing experiments with fresh toluene for bitumen, maltene, and asphaltene films were performed. Bitumen, maltene, and asphaltene films were found to behave differently at the toluene/water interface. For future work, it would be interesting to study the interfacial behaviour of bitumen and asphaltene at high concentrations, as well as interfacial behaviour of maltene and asphaltene subfractions. More detailed study of the material remaining at the interface after washing of bitumen film with toluene, material re-adsorbed from the recovered top phase toluene upon contact with fresh water and surface active material found in process water is of great interest for the future work. The material of interest transferred onto a solid substrate by Langmuir-Blodgett deposition can be further characterized using Fourier transform infrared (FTIR) spectroscopy.